# Primordial radionuclides in pit lakes in Sweden

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Cover illustration: Photograph of Kvinnersta kalkbrott

I would like to dedicate this work with reverence

to my Creator, my God, my Heavenly Father.

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## Abstract

In Sweden, there are many pit lakes, originating from limestone quarries and metal mines, with unknown status in regard to the activity concentration of radionuclides. Such knowledge is generally available only for pit lakes from uranium mining activities. However, since naturally occurring radionuclides such as $^{238}$U, $^{232}$Th and $^{40}$K are always present in the environment, is it possible that, for example, a copper mine might contain radioactivity levels to warrant concern? For non-uranium mines, which characteristics are typical among those that contain higher amounts of radionuclides, and how should such characteristics be determined? These are some of the questions that are dealt with in this work.

In the course of this work, radiochemical procedures were set up and validated, and sampling of pit lake water and sediments were carried out and analyzed by gamma and alpha spectrometry, mass spectrometry and fluorescence techniques. Statistical analyses were employed to explore similarities among the different pit lakes. One site was more thoroughly studied for vertical distribution of water quality parameters, stable elements and radionuclides.

All of the pit lakes in this work had an activity concentration of naturally occurring radionuclides well below the recommendations for drinking water. Furthermore, the activity concentrations found in lakes in Northern Sweden were about a factor of ten lower for U isotopes and a factor of three lower for $^{210}$Po and Th isotopes, compared to the southern part of Sweden. This geographical contrast coincided with the difference in ambient dose equivalent rate that was measured at each site, where the higher dose rates were found in the southern part of Sweden. Furthermore, in a stratified lake, the concentration of stable elements and radionuclides in the surface water were many times lower than the concentration found in the deeper part of the lake. Thus, the concentration measured in surface water ought to be viewed as an underestimation of the average concentration in a pit lake.

# Sammanfattning på svenska

Gruvindustrin har varit betydande för Sveriges ekonomi under lång tid, detta tack vare den mineralrika berggrunden, de stora skogstillgångarna samt den tidiga användningen av masugnar, redan från 1100-talet. Idag är endast ett fåtal gruvor aktiva, men lämningarna efter Sveriges gruvhistoria kvarstår genom de gruvhål som återfinns över hela landet. När en gruva tas ur bruk kommer gruvhål som är belägna under grundvattennivån att fyllas av grundvatten upp till grundvattennivån, vilket skapar en så kallad gruvsjö, *pit lake* på engelska.

Den många gruvsjöar som finns i Sverige härrör från brytning av sten, mineraler och metaller. Eftersom både uran och torium samt andra naturligt förekommande radionuklider finns i berggrunden, kommer de att finnas med i gruvprocessens alla steg. Halten av naturligt förekommande radionuklider i och runt gruvsjöarna är i de flesta fall okänt. Vidare saknas kunskap om hur dessa radionuklider och olika grundämnen är fördelade i gruvsjöar från gruvor och stenbrott i olika delar av landet, liksom vilken stråldos man erhåller då man vistas vid gruvsjöar. Dessa är frågorna som behandlas i denna avhandling.

Tillvägagångsättet bestod i att samla prover från ytvatten och ytsediment från ca 50 gruvsjöar och analysera koncentrationen av flera grundämnen och radionuklider i dessa prover, samt att mäta stråldoser (miljödosekvivalentrat) vid samtliga gruvplatser. Denna data användes därefter i statistiska analyser för att undersöka vad som skiljer olika gruvsjöarna åt och vilka likheter som finns för samma typ av gruva. En av de studerade gruvsjöarna valdes därefter ut för att studera hur flera av de tidigare uppmätta parametrarna varierar med vattendjupet i sjön.

Sammanfattningsvis visar denna avhandling att samtliga gruvsjöar som studerades hade urankoncentrationer i ytvattnet som var jämförbara med motsvarande i grundvatten i Sverige. Gruvsjöarna med de högsta urankoncentrationerna i ytvattnet fanns i södra delen av Sverige, där främst granitbrotten hade de högsta värdena. Dessa gruvplatser uppvisade också de högsta miljödosekvivalentrat-värdena på 0,15 – 0,30 µSv/h. Slutligen visade resultaten att i en sjö med skiktade vattenlager kan koncentrationen av radionuklider vara uppemot en faktor sex högre vid botten jämfört med ytvattnet, och att denna koncentrationsökning sammanföll med liknande ökning av koncentrationen av järn och mangan.

# List of papers

This thesis is based on the following studies, referred to in the text by their Roman numerals.

I. Mantero, J, Thomas, R, Isaksson, M, Forsell-Aronsson, E, Holm, E, García-Tenorio, R. **Quality Assurance via internal tests in a newly setup laboratory for environmental radioactivity**. JRNC (2019) 322: 891-900. Reprinted by permission of JRNC

II. Mantero, J, Thomas, R, Holm, E, Rääf, C, Vioque, I, Ruiz-Canovas, C, Garcia-Tenorio, R, Forsell-Aronsson, E, Isaksson, M. **Levels of natural radioactivity and heavy metals in pit lakes from Southern Sweden**. Submitted

III. Thomas, R, Mantero, J, Ruiz-Canovas, C, Holm, E, García-Tenorio, R, Forsell-Aronsson, E, Isaksson, M. **Levels of natural radioactivity and heavy metals in pit lakes from Northern Sweden**. Manuscript.

IV. Thomas, R, Piñero García, F, Forsell-Aronsson, E, Holm, E, Mantero, J, Isaksson, M. **Natural radioactivity and heavy metal distribution in pit lakes in Sweden analysed by principal component analysis**. Manuscript.

V. Thomas, R, Mantero, J, Perez-Moreno, S, Ruiz-Canovas, C, Isaksson, M, Forsell-Aronsson, E, Holm, E, García-Tenorio, R. **$^{226}$Ra, $^{210}$Po and Lead isotopes in a pit lake water profile in Sweden.** Submitted

# Content

# 1   Introduction

Lakes can be classified as one of eleven major types, which can be further divided into 76 subtypes. The 11 categories of lakes are: tectonic, vulcanic, landslide, glacial, solution, fluvial, aeolian, shoreline, organic, meteorite and anthropogenic lakes [1]. This thesis focuses on the latter lake type, specifically on pit lakes resulting after mine closure. With intentions to review the similarities and differences among them and their content in regard to primordial radionuclides.

## 1.1 Formation of a pit lake

The mining process starts with a prospecting method of choice, a common approach involves drilling in the bedrock and analyzing the extracted core. The actual mining can be done using different methods depending on the area and location of the ore; two common methods are open pit and underground mining. During active mining, ground water is removed by pumps to allow excavation below the original groundwater table. When mining ends at an open pit, it may be backfilled with mining material. However, in some cases, back-filling an open pit may be unpractical and costly. Therefore, the pits may be left open and allow inflow of groundwater and surface water to fill up the pit. A steady water surface will be established when the lake surface recovers to the local groundwater table – and a pit lake is created (Figure 1).



Figure 1 Two photos of open pit mines in Sweden during two stages. The larger photo shows a newly closed mine where water is seeping through the ground and cracks in the wall (darker areas in the middle of the photo). The smaller photo shows a fully developed pit lake

## 1.2 Characteristics of pit lakes

There are a few but important characteristics of pit lakes that separate them from natural lakes from a chemical, physical and biological standpoint and these differences in characteristics will be discussed below. The natural lakes most similar to pit lakes are crater lakes [2].

### 1.2.1 Geology

The mining sites are chosen after determining if there is enough mineralization for the mining to be profitable, resulting in pit lakes being situated in areas with a high concentration of certain ores. However, the amount of waste rock that needs to be excavated to obtain the desired ore can be many times larger than the desired ore itself. A quantitative measure for determining the profitability is the stripping ratio, e.g. a ratio of 2 indicates that for each ton of ore, 2 tons of waste rock are generated. Stripping ratios of 3.7 for coal mine, 1 for limestone and 0.9 for iron mine have been reported [3], while up to 90% of waste rock can be expected for lead and zinc mines [4].

As these ores and waste rocks are unearthed, oxidation-reduction processes take place, combined with leaching of the minerals through interaction with water. A well-studied ore in this regard is pyrite, $FeS_2$, in which the oxidation of sulfur can lead to production of sulfuric acid. Once this process starts, the sulfuric acid will further leach the host rock, exposing more of the sulfur, leading to accelerated oxidation and creation of more sulfuric acid [4-9]. This chemical process is called acid mine drainage and the chemical reaction is [7]

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (Eq.1)$$
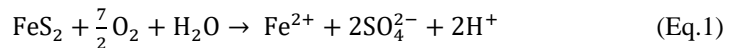
This reaction can proceed, although to a limited degree, even without the presence of molecular oxygen since the oxidized ferric iron, $Fe^{3+}$, will further oxidize the pyrite, creating sulfuric acid and acidity [9]

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (Eq.2)$$
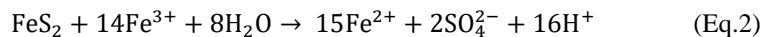
The finer the particle size of the mining waste, the larger is the relative surface area and thus a higher risk for acceleration of the chemical reaction. It is also important to note that this dissolution of pyrite will release other accompanying metals in the host rock. The addition of carbonate minerals, by e.g. liming can help to neutralize or decelerate the acid generation.

However, liming can facilitate the solubility of metals as oxyanions, where As, Sb, Mo and Se has been released in concentrations on the order of mg/L from waste rocks even at slightly alkaline conditions [10].

Further, neutralizing only the lake water might not prevent high concentrations of metals in the lake, since another source of acidic water is the oxidation of pyrite in the heaps of waste rocks surrounding the pit lake. This can supply the lake body with acidic water and metals as the rain wash the rock piles and transport the metals into the lake by surface water runoff.

## 1.2.2 Physical shape

The remaining pit formed by the excavation can take the shape of a downward pyramid with steep walls and relatively small bottom area compared with the overall excavated area. This typical shape differs from natural lakes, which tend to have gradual slopes and relatively shallow depths. This difference can be quantified through the parameter relative depth, $D_r$, which is proportional to the ratio of the maximum depth of the lake to the mean diameter

$$D_r = \frac{D_{max} * \sqrt{\pi}}{20 * \sqrt{A}} \qquad \text{(Eq.3)}$$

where $D_{max}$ is the maximum depth in meters and A is the surface area of the lake in km$^2$ [11]. This parameter can be used to predict the stability of stratification in lakes where typical values for pit lakes range between 10% and 40%, and are less than 2% for natural lakes [12]. A higher $D_r$ also means that the wind movement will cause the water column to mix to a lesser extent.

Despite pit lakes having relatively large depths and being prone to exhibit stratification layers, the relatively homogenous water (i.e. mainly groundwater) can still result in well mixed water. In contrast, lakes which are supplied with chemically different water, such as river water and groundwater with different salinity, can exhibit stratification layers due to the difference in density [13].

## 1.3 Sediment

Sediments are matter such as silt, clay, organic debris and other chemically precipitated particles that fall down and accumulate at the bottom of water bodies. For natural lakes, these sediments tend to be mostly organic matter due to the biologically active water, while in pit lakes, the biological activity can be much lower or non-existent. The sediments, if any, are therefore usually consisting of fine particles caused by the mining activity i.e. they are minerogenic.

Another relevant process in pit lakes with pH around 8, and for oxidizing conditions, is the precipitation of Fe and Mn hydroxides, which act as efficient scavengers adsorbing other elements and causing them to co-precipitate. Once precipitated, and in reducing conditions, Fe and Mn hydroxides can re-dissolve and release the adsorbed elements. There can also be transportation of elements within the sediment itself caused by changes in redox (reduction-oxidation-reaction) potentials where Fe and Mn can be transported from the deeper, reducing, part of the sediment to the oxygenated surface sediment where they can be re-precipitated [14].

Collectively, the sediment represents both the biological and chemical activity taken place in the lake, and the inflow of particles washed down from the surroundings by the surface water runoff. Thus, it is an important sample to analyze, where the deeper sediment can provide information of the history of the lake and surface sediment of the freshly settled particles, respectively.

Furthermore, if both the water and sediment are analyzed with regard to their composition, the distribution coefficient $K_d$, which is an important model parameter, can be determined. $K_d$ is defined as the ratio between contaminant concentration associated with the solid phase and the contaminant concentration in the aqueous solution, when the system is at equilibrium. This parameter is defined in such a way that in order to correctly apply it, six assumptions have to be made. Firstly, the contaminant in question is present in trace amount in both the aqueous and solid phases. Secondly, there exists a linear relationship between the amount of contaminant in the aqueous and solid phase. Thirdly, equilibrium conditions exist, meaning that the rates of forward and reverse chemical reactions have reached a steady state. Fourthly, the kinetics (rates of chemical reactions) of rapid desorption and adsorption are equal. Fifthly, it defines the sorption of one contaminant and one sorbent. Lastly, all adsorption sites are possible and have equal strength [15].

Some of these assumptions are somewhat interconnected, since a high concentration of contaminant in the aqueous solution or a limited number of adsorption sites will result in a saturation (plateau), i.e. a non-linear relationship. There are other parameters apart from $K_d$ that describe the relation between the aqueous and sorbed concentration; these are collectively named sorption isotherms. The two most common nonlinear isotherms are derived from the Freundlich and Langmuir model equations [16].

## 1.4 Water quality parameters

A relatively simple way to get an overview of the water quality parameters in a lake is by using a water probe. Common parameters measured by such a probe are pH, redox potential (ORP), specific conductance (SC) and dissolved oxygen concentration (DO) among others. Measuring these parameters along the lake depth will also provide information on possible lake stratifications.

pH is the negative base 10 logarithm of the hydrogen ion concentration in moles per liter. pH plays an important part in the hydrolysis of metal ions (Eq.4) where a higher pH increases the rate of hydrolysis to $M(OH)^{z-x}$, while a lower pH increases their solubility as $M^{z+}$ [17-19] where z is the charge of the metal

$$M^{z+} + xH_2O \leftrightarrow M(OH)^{z-x} + xH^+ \qquad (Eq.4)$$
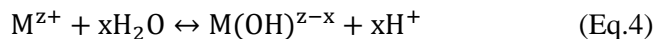
ORP (unit: mV) is a measure of the oxidizing or reducing potential of the water and is an important parameter in understanding the chemical behavior of elements, since their chemical behavior depends on their oxidation state. In natural lake systems, redox is mainly controlled by oxygen and organic matter, where atmospheric oxygen is dissolved (saturated) in the surface water and is depleted through biota respiration and decomposition of organic matter throughout the lake depth. In surface water common redox potentials are +200 mV to +800 mV and in deep groundwater around -400 mV to -200 mV [18].

SC (unit: μS/cm) is the measure of the conductivity of the water and can be used as an indicator for the concentration of dissolved ions in the water. Since the conductivity is temperature dependent, the parameter is usually recalculated by the water probe to a reference temperature, usually 25 °C.

DO (unit: mg/L) is important for the sustainability of aquatic organisms and should be above 8 mg/L for good water quality. DO is dependent on temperature, and the warmer the water the less amount of oxygen can be dissolved. The saturation concentration for natural water is 14.7 mg/L at 0 °C and 8.3 mg/L at 25 °C [20].

Another water quality parameter that is relevant in terms of the chemical composition is alkalinity, which is the water's capacity to accept protons, i.e. the buffering capacity, or capacity to neutralize acidity. The alkalinity is mainly due to bicarbonate ions which are the main anions in most fresh water systems with neutral pH. However, bicarbonate can further dissociate to carbonate ions, which readily complexes metals and can increase their solubility [18].

## 1.5 Lake stratification

Lake stratification is the result of limited or non-vertical water mixing due to different physical and chemical properties of the water layers. Two common stratification layers are thermocline and chemocline. The chemocline signifies the layer where differences in oxygen concentration, sulfide concentration and redox potential show a more or less steep gradient [21]. The thermocline is a more or less steep temperature gradient that separates the water layers due to density differences caused by differences in temperatures. This is a common cause of stratification in lakes during summer and winter, where the differences in temperature between surface water and bottom water can be the highest. In the seasons spring and fall, the increase and drop of outside temperatures respectively, reduces the temperature differences between the water layers and can cause them to mix, clearing any stratification. This is collectively termed seasonality effects.

In the simplest case, if a lake exhibits no stratification, a simple surface water sample would be a representative sample of the lake body as a whole. For unknown lakes or lakes known to exhibit stratification, one could sample surface water during e.g. spring or fall when the water is usually mixed in order to have an idea of the concentration of various elements in the water. This could provide a useful strategy for screening purposes.

The stratification of lakes is not necessarily undesired. For heavily contaminated pit lakes, stratification could result in high concentration of metals and radionuclides in the lower part of the lake. If biological activities or organic matter are introduced in the top layers, continuously supplying organic matter to the bottom, then this can help to sediment the contamination.

## 1.6 Radionuclides and elements

Since the discovery of uranium by Martin Klaproth in 1789 and its invisible penetrating rays by Henri Becquerel in 1896, scientists started to conduct worldwide surveys of radioactivity in the early 1900s. Soon they discovered that radioactivity was not as rare in the environment as previously believed. The discovered elements were categorized both by their physical properties, such as radiation emitted and their decay rates, and also by their chemical properties. The latter included experiments studying the radionuclide's tendency to deposit on various metals, a process called electroplating, where the results categorized the radionuclides according to the element they closely resembled. Another procedure was the radionuclide's tendency to precipitate along with a known element; if the precipitate contained radioactivity then the radionuclide would behave chemically similar to the known element [22].

Uranium, radium and thorium were the first studied radionuclides and were extracted from the ore pitchblende (uraninite). These radionuclides can be found in many other minerals and at the time of writing this thesis, there are 281 minerals associated with uranium and 25 associated with thorium [23]. In regard to their abundance on Earth, uranium is the 44th most abundant element and thorium the 37th [22].

Through joint efforts of the laboratories of Frederick Soddy and Ernest Rutherford, the displacement law of radioactivity was published in 1913, which expressed the position of radionuclides and their decay products in the periodic table. Thus, the radionuclides found together with uranium and thorium were understood to originate from the decay series of $^{238}$U, $^{235}$U and $^{232}$Th. In 1906 Norman Campbell and Albert B. Wood discovered radioactivity in potassium, later understood to be the isotope $^{40}$K.

$^{238}$U, $^{235}$U, $^{232}$Th and $^{40}$K are commonly known as the naturally occurring radionuclides and materials containing them are termed NORM. To further categorize NORM, the acronym TENORM can be used to distinguish the technologically enhanced NORM, where TENORM can be the product (intentions to increase the concentration) or byproduct (without intentions). Such processes can be found in the mining industry. For biological processes that enhances the radionuclide concentration the acronym BENORM can be used [24].

## 1.7 Detection of radionuclides

Identification of a radionuclide is performed through spectroscopy, where the preferred method depends on the type of radiation emitted, mass or activity concentration of the radionuclide in the sample and the desired detection limit. The detection limit in spectroscopy is a statistical quantity that takes into account the background or the surroundings of a peak of interest, and the efficiency to detect that peak. Generally, if the activity is sufficiently high compared to other radionuclides in the sample, and with energies that can be well separated from the rest, radiation-based techniques are employed. Otherwise the mass to charge ratios, determined by mass spectrometry, is employed. The radiation-based techniques most often used, are alpha, beta and gamma spectrometry for the detection of alpha and beta particles and gamma rays respectively. The use of chemistry can help to decrease the detection limit by concentrating and isolating the element of interest from other interfering elements, and for radionuclides this science is referred to as radiochemistry. Detection of alpha and beta particles requires in most cases a radiochemical procedure.

Most radionuclides in the environment can be found originating from the $^{238}$U, $^{235}$U and $^{232}$Th series, and the emitted radiation in these decay chains includes alpha, beta and gamma radiation. For example, the alpha emitters in these series are $^{234,235,238}$U, $^{227,228,230,232}$Th, $^{223,224,226}$Ra, $^{219,220,222}$Rn, $^{210,212,214,215,216,218}$Po, $^{209,211,212}$Bi, $^{231}$Pa and $^{227}$Ac. The quantification of most of these alpha emitters is simplified by their relatively short half-life, causing them to be in equilibrium in regard to their activity concentration with their source. Furthermore, radionuclides with half-lives on the order of hours or less are difficult to measure considering transportation, sample preparation and measurement time needed.

Among the publications found on lake and river water, the most commonly studied radionuclides are $^{238}$U, $^{226}$Ra and $^{210}$Po. The former mainly due to its solubility and relatively high abundance which enables its determination by mass concentration. The latter two because of a combination of both being relatively common in the environment (due to the source $^{238}$U), but also due to their importance in regard to radiation exposure. However, their mass concentration compared to their activity concentration is much less than that for $^{238}$U and thus radiometric techniques are employed for $^{226}$Ra and $^{210}$Po.

Activity concentrations that can be expected to be found in Swedish groundwater (and to some extent in pit lakes) regarding $^{238}$U are mostly below 5 µg/L, according to Geological Survey of Sweden (SGU). The SGU survey included 2875 measurements points and 49% were below 5 µg/L, while 15% were equal to or higher than 30 µg/L [25]. These two quoted concentration levels correspond to about 60 mBq/L and 360 mBq/L of $^{238}$U, respectively (1 ppm of $^{238}$U corresponds to 12.35 Bq/kg). Regarding $^{210}$Po, one study surveyed 328 drilled bedrock wells where the activity concentration varied between 8.5 and 950 mBq/L, where the highest concentration was found in granite and granodiorite bedrock [26]. The activity concentration in Swedish soil is about 70 Bq/kg for $^{238}$U and 34 Bq/kg for $^{232}$Th [27], and in Swedish bedrock, from 18 sites and 777 measurements, 8-27 ppm and 8-90 ppm for $^{238}$U and $^{232}$Th, respectively [28]. The latter corresponds to about 99-303 Bq/kg for $^{238}$U and 32-360 Bq/kg for $^{232}$Th, respectively (1 ppm of $^{232}$Th corresponds to 4.1 Bq/kg).

# 2 Aims

The overall aim of this work was to increase the knowledge on the activity concentration of naturally occurring radionuclides that can be found in Swedish pit lakes originating from non-uranium mines, and how the activity concentrations relate to the concentrations of elements and water quality parameters.

The specific aims were to

1) Set-up, implement and test the quality assurance of the methods to be used in this work
   **Paper I**

2) Study concentration of radionuclides, alkali and alkaline earth metals, transitional and post-transition metals in samples of surface water and surface sediments from pit lakes throughout Sweden
   **Papers II and III**

3) Perform statistical analysis on the obtained data from II-III to explore relations between parameters
   **Paper IV**

4) Study the vertical distribution of parameters along the depth of one pit lake
   **Paper V**

# 3 Material and methods

## 3.1 Project plan and strategy

The first step in this work was the implementation and quality assurance of the methodologies to be used in this work, including gamma and alpha spectrometry for the measurements of naturally occurring radionuclides (paper **I**).

The second step was the mapping of mining sites across Sweden that contained a pit lake. This was achieved through browsing web sources and literature, and through personal communications with mining companies and SGU. Altogether, 40 mining sites were chosen, which covered large areas of Sweden, from Malmö in the south to Kiruna in the north. In order to build up baseline data and to obtain an overview of the concentration of elements and radionuclides in pit lakes, surface water was collected and at some sites, whenever possible, also surface sediments (paper **II**, **III**).

The third step was to perform statistical analyses on all the data in order to explore relations among the examined quantities, and to investigate if any similarities were found for similar types of mining sites (paper **IV**).

Lastly, a pit lake with a relatively large depth was chosen to study the vertical distribution of several parameters along the depth. The results were then compared with those found in surface water in order evaluate how representative a surface water sample can be (paper **V**).

Sampling was performed in April, June and October 2015 (paper **I-IV**) and in April 2016 (paper **V**).

## 3.2 Sample collection and preparation

Surface water was collected with a bucket attached to a rope thrown out towards the middle of the lake and reeled in to obtain a sample further away from the shore, since shallow waters are likely to contain a higher concentration of resuspended particles and debris. The amount of water collected with the bucket was either 5 L or 10 L. For sampling along the lake depth, a 5 L Niskin bottle (General Oceanics Inc, USA) was used from the side of an inflatable boat at the deepest part of the lake.

Water samples were poured into 5 L Fisherbrand™ plastic jerry containers (Fisher Scientific, USA) and concentrated nitric acid was added until pH was below 2, in order to reduce adsorption to container walls, microbial activities and precipitation by keeping the metals soluble. Water samples for the determination of stable elements were filtered with a filter paper of pore size 35-40 µm while water samples for the determination of radionuclides were only filtered (35-40 µm) if visible debris was found in the water container. In most cases, the water to be analyzed by alpha spectrometry was not filtered. The water was not filtered prior to the acidification in order to study the concentrations in unfiltered water, i.e., filtration was done after acidification to remove larger particles still remaining in solution. Thus, despite water samples sent to ICP-MS were filtered with a 35-40 µm filter paper, the results could include elements originally found in particles larger than 35-40 µm due to dissociation caused by the acidification.

Surface sediments were collected manually with a shovel from the shore whenever possible. Approximately 1 kg of wet weight was collected and comprised of the top 1 cm layer. Some pit lakes had too steep walls and no accessible shore and at other sites the sediments comprised mainly of gravel and rocks and thus no sample could be collected at these sites.

Rocks surrounding the pit lakes were collected at some sites with dose rates roughly twice the average background in Sweden (average considered to be 0.13 µSv/h). Surface sediments and rocks were stored in plastic zip bags until further sample preparation, which included drying, grinding, homogenizing and sieving to obtain the <1 mm fraction for further use.

## 3.3 Site characterization

The mining sites chosen in this work comprised of limestone, marble, feldspar, granite and stone quarries, and Fe, Cu, Zn, Ag and Au mines. Some sites could not be characterized, since no information was available on the type of mine or excavated ore. The sites were chosen on the basis of two criteria: 1) to cover a large geographical area of Sweden, and 2) to include areas with higher activity concentration of radionuclides. As basis for the latter criterion, maps of the concentration of U, Th and $^{40}$K in the ground from airborne measurements of Sweden performed by SGU were used [29].

Ambient dose equivalent rate, $\dot{H}^*(10)$, was measured at the mining sites with a radiation detector SRV-2000 (RADOS, Finland) at a height of one meter above ground after allowing the instrument to collect an average value of a minimum of five minutes. This instrument consists of two energy compensated Geiger-Müller tubes with energy range from 50 keV to 3MeV and a dose rate range from 0.05 µSv/h to 10 Sv/h.

A pit lake chosen for the study of vertical distribution of water quality parameters and elements were sampled from an inflatable boat to access the deepest part of the lake. This point was located with the sonar Helix 5 SI which was used together with the software Autochart Pro (Humminbird, USA) to produce bathymetric maps.

## 3.4 Water quality parameters

Along with surface water sampling, the water quality parameters pH, redox potential (ORP), specific conductance (SC) and dissolved oxygen level (DO) were measured with a water probe submerged into the lake, YSI Professional Plus (Xylem Analytics, USA). For measurements of these parameters along the lake depth, the probe Hydrolab MS5 (OTT HydroMet, Germany) was used. The probes were calibrated one day prior to the sampling with certified solutions purchased from the supplier.

## 3.5 Stable elements

Apart from the radionuclides mentioned in the following subchapter, the stable elements of interest included Na, Mg, Al, P, S, K, Ca, Fe, Mn, Cr, Cu, Zn, As, Sr, Ba and Pb. These elements were chosen primarily to cover the element groups non-metals, transition and post transition metals, and alkali and alkaline earth metals. The study of several alkali metals and alkaline earth metals allows the comparison of concentrations for the same group of elements with increasing atomic number.

Fe and Mn were chosen due to their sensitivity to redox potentials which controls their fate, resulting in either precipitation or dissolution, which in turn can affect mobility of other elements through co-precipitation. S and P were included since they are important in the growth and metabolism of organisms and could be an indicator of increased microorganism activity in the lakes, which could explain e.g. rapid depletion of oxygen with water depth. Cr, Cu, Zn, As and Pb were included due to their toxicity to aquatic life and human health when in sufficiently high concentrations and certain chemical states.

### 3.5.1 ICP-MS

The concentrations of elements in water samples were measured by an inductively coupled plasma mass spectrometer (ICP-MS). During this work, two systems were used, during 2015 an Agilent 7500c and later this system was upgraded to ICP-MS/MS Agilent 8800 (Agilent Technologies, Japan). These analyses were performed at CITIUS laboratory (University of Seville, Spain). Apart from previously mentioned elements, Th and U were also measured by ICP-MS. The results obtained were semi-quantitative covering a large number of elements with few blanks between each sample batch. This results in a higher uncertainty for the reported elements, however, for the purpose of obtaining an overview, this was a reasonable compromise in order to reduce costs and to manage a large number of samples.

### 3.5.2 XRF and SEM-EDX

The concentration of elements in surface sediments and rocks was measured with a wavelength dispersive x-ray fluorescence (WDXRF) detector system, Axios (Malvern Panalytical, United Kingdom). For a few selected rock samples an energy dispersive x-ray spectroscopy (EDX) probe coupled with a scanning electron microscope (SEM) were used to study the concentration of elements at various spots and to obtain morphology images of the sample surface. These analyses were performed at CITIUS laboratory (University of Seville, Spain). The back scattered electron images (BEI) reflected the atomic number of the different elements present at the sample surface, which provided a visualization of the inhomogeneity present in sample sizes in the µm range. The SEM-EDX detector system has an energy resolution of 137 eV at 5.9 keV (JEOL 6460 LV, USA) and the elements analyzed included C, O, Na, Al, Si, P, K, Ca, Ti, Mn, Fe, Y, Zr, Nb, Yb, Ta, W, Th and U.

## 3.6 Naturally occurring radionuclides

In the decay series of $^{238}$U, $^{235}$U and $^{232}$Th, a total of 47 radionuclides are included from 13 different elements, with Po and Th being the most common elements appearing seven and six times, respectively. Considering a gap of two months' time from the start of sampling to measurements of the collected samples (including transportation, sample preparation and measurements time), some radionuclides will be in equilibrium with their source due to their relatively short half-life.

Below are given the decay series of $^{238}$U, $^{235}$U and $^{232}$Th, showing only those radionuclides with a half-life comparable to, or longer, than two months. The radionuclides in bold are those that can readily be analyzed by alpha or gamma spectrometry. For the latter, with the criteria that the gamma rays have an energy above 40 keV and intensity higher than 1%. This is because in most environmental samples, assuming no enhancement in the activity concentration, only the gamma lines above 40 keV with intensity above 1% are usually visible with a conventional gamma detector of high purity germanium with lead shielding.

**$^{238}$U** → **$^{234}$Th** →//→ **$^{234}$U** → **$^{230}$Th** → **$^{226}$Ra** →//→ **$^{210}$Pb** →//→ **$^{210}$Po** → $^{206}$Pb (stable)

**$^{235}$U** →//→ **$^{231}$Pa** → **$^{227}$Ac** → //→ $^{207}$Pb (stable)

**$^{232}$Th** → **$^{228}$Ra** →//→ **$^{228}$Th** →//→ $^{208}$Pb (stable)
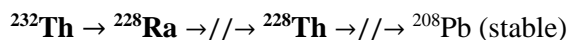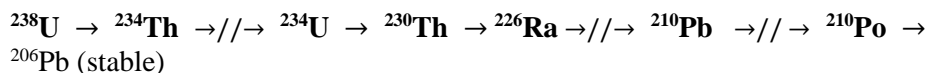
As can be seen, utilizing both alpha and gamma spectrometry covers all of the relevant radionuclides in all three decay chains. Among the above radionuclides, $^{234,235,238}$U, $^{228,230,232}$Th, $^{226}$Ra and $^{210}$Po can readily be measured by their alpha particle emission, while the rest are better detected by their photon emission.

In this work, alpha spectrometry was employed for water, surface sediment and rock samples and gamma spectrometry for surface sediment and rock samples. Although beta spectrometry could be employed, the resulting need for another radiochemical procedure for beta emitters was determined not feasible due to the high sample throughput offered by gamma spectrometry. However, one important consideration between these radiometric techniques are their sensitivity, which can be expressed as the minimum detectable activity (MDA). The lower the MDA, the lower activity concentration is possible to be detected with the detector system. In general, between these three radiometric techniques, the lowest detection limit can be achieved by alpha, then beta and lastly by gamma spectrometry.

## 3.6.1 Gamma spectrometry

For gamma spectrometry, the sample preparation included homogenizing, drying and pulverizing the solids to a fraction size less than 1 mm. The samples were then packaged in cylindrical containers of 35 ml (Nolato Hertila, Sweden) and vacuum packaged with a vacuum sealer (OBH Nordica, Sweden) and sealed with polyethylene vacuum bags, to minimize radon losses.

The containers were placed close to the detector and usually measured for more than 24 h. The detector used was a germanium p-type extended range coaxial detector, (GX4020, Canberra, USA) with a relative efficiency of 37.1 % and a resolution of 1.76 keV at 1332 keV. The detector was shielded with 10 cm lead and coupled with a plastic scintillator BC-418 (Saint-Gobain Crystals) working in anti-coincidence to further reduce the Compton continuum background caused by cosmic rays [30]. These analyses were performed at the University of Seville. Energy and full-width-at-half-maximum calibration was performed on each spectra and efficiency calibration was performed by measurement of the reference materials IAEA-RGU-1 and IAEA-RGTh-1 [31].

To correct for differences in atomic composition and density between the reference materials and the sample, transmission measurements were performed to calculate the self-absorption effects. This was done with point sources of $^{137}$Cs, $^{210}$Pb, $^{133}$Ba and $^{57,60}$Co covering the energy rangy from 35 keV to 1332 keV. The point sources were first placed on top of the reference material and then on the sample, and the resulting net counts were used to calculate a ratio, R (net counts from sample to net counts from reference sample). This ratio was used to determine the correction factor $C_{selfabs}$ [32, 33].

$$C_{selfabs} = \frac{1 - {}^1/_R}{\ln(R)} \qquad (Eq.7)$$

Self-absorption is more severe for the lower energies, up to around 200 keV, and the severity increases with container height, effective atomic number of the matrices and density. $C_{selfabs}$ was used to correct the efficiency, $\epsilon_\gamma$, in order to get a more accurate activity concentration, A

$$A = \frac{N}{C_{selfabs} * \epsilon_\gamma * \gamma * t * m} \qquad (Eq.8)$$

where N and $\gamma$ is net count and intensity of the gamma ray, respectively, *t* is the measurement time in seconds and *m* is the mass in kg.

For naturally occurring radionuclides, the activity concentration was calculated by taking the ratio of the activity concentration of the reference material (IAEA-RGU-1 and IAEA-RGTh-1) to the sample. This will result in that the intensity $\gamma$ will cancel out and there is no need to use this value and its associated uncertainty. Similarly, as the emitted gamma ray energies are the same in the reference material as in the sample, there is no need to perform a polynomial curve fitting for the efficiency (with an added fitting uncertainty). Also, there is no need to perform a true coincidence summing correction [34].

To estimate $^{226}$Ra by gamma spectrometry, the sample container was stored for a minimum of four weeks to allow ingrowth of $^{222}$Rn and the progenies $^{214}$Pb and $^{214}$Bi, so that an equilibrium between the radionuclides would be achieved. Thus, one Becquerel (Bq) of $^{214}$Bi, $^{214}$Pb and $^{222}$Rn corresponds to one Bq of $^{226}$Ra. $^{214}$Bi and $^{214}$Pb are chosen since they have gamma rays free of interferences and with sufficiently high intensities.

### 3.6.2 Alpha spectrometry

The chemical behavior of a radioisotope can be assumed to be identical with that of other corresponding isotopes of the same element. The chemical separation methods of radionuclides are based on similar methods used in other fields of chemistry, namely precipitation, liquid extraction and ion exchange [18].

To assess the activity concentration by alpha spectrometry, the chemical analogue to the element of interest (called tracer) was added to the sample as early as possible in the preparation procedure, to include all potential losses during sample preparation in a similar manner. The tracer was added in similar amount to the expected activity of the radionuclide of interest in the sample, which was about 50 mBq for U isotopes. Since the tracer activity is known, and assuming similar chemical behavior, the yield, Y, of the chemistry procedure can be calculated

$$Y = \frac{NetCPS}{\epsilon_\alpha * A_{Tr}} * 100\ \%$$ (Eq.9)

where NetCPS are the net counts per second from the sample and $A_{Tr}$ is the activity of the added tracer in Bq. The efficiency, $\epsilon_\alpha$, includes both the probability of absorbing alpha particles once they enter the detector volume (intrinsic efficiency) and a function of detector diameter and distance from the source (geometric efficiency). The former is assumed to be constant for the range of energies analyzed in this work (4-8 MeV), since alpha particles once entering the detector volume can be assumed to be fully absorbed due to their high ionizing density.

Then, the activity of the isotope, $A_{Iso}$, can be calculated relatively easy,

$$A_{Iso} = \frac{NetCPS_{Iso}}{NetCPS_{Tr}} A_{Tr} \qquad \text{(Eq.10)}$$

since measurement time and efficiency are the same for both the tracer and isotope of interest. The intensity of the emission as mentioned in Eq.8, $\gamma$, is set to 1, since NetCPS includes all the emitted alpha particles (counts) for a particular isotope.

The radiochemistry required for alpha spectrometry comprised the bottleneck in this work. In order to increase sample throughput, [226]Ra in surface water was only measured in a few samples, since it required a separate radiochemical procedure. [210]Po, U and Th isotopes were measured in all samples and the tracers used were [232]U, [229]Th (and progeny [225]Ra) and [209]Po.

One method capable of efficiently concentrate these radionuclides of interest in water, is by co-precipitation with Fe hydroxides. These are known to be efficient sorbents (scavengers) with a high surface to volume ratio, up to 348 $m^2g^{-1}$ [35]. When the pH of the solution is raised to around 8, the Fe hydroxides, $Fe(OH)_3$, forms sparingly soluble precipitates leaving behind anionic components and alkali and alkaline earth metals in solution [18]. Thus, iron hydroxides were chosen for the preconcentration step.

The mass of water sample used to analyze [210]Po, [226]Ra, U and Th isotopes was about 500 g and about 1 g for dried surface sediments and rocks. Some experiments were conducted for surface sediment samples where two digestion procedures were compared (paper **I**): 1) open digestion with the acids $HNO_3$ and HCl (ratio 1:3, aqua regia) in a glass beaker with a glass lid at a temperature around 80 °C and stirring for approximately 24 h, and 2) total digestion with HF acid through microwave assisted digestion. The differences in these two are that open digestion allows for larger sample sizes to be digested, with up to several grams compared with 250 - 500 mg per vessel with microwave digestion.

However, the latter method is more efficient, since the pressurized microwave vessels with temperatures close to 200 °C are capable to digest a sample more thoroughly and in a shorter time, especially since HF acid is capable of breaking up the Si-O bonds in the sample lattice. Samples digested with HF had to undergo an additional procedure with the addition of boric acid to complex and neutralize the fluorine through fluoroboric acid ($HBF_4$). Furthermore, microwave assisted digestion reduces the amount of acid used and prevents large amounts of acid fumes and also loss of radionuclides through evaporation. Thus, microwave assisted digestion was the main method of digestion for surface sediments and rocks.

Once a sample had been digested, it was diluted with distilled water to about 500 mL and then proceeded as a water sample. $^{210}$Po, U and Th isotopes were analyzed following the procedure outlined in paper **I**. Ra isotopes were co-precipitated with $MnO_2$, purified by anion and cation exchange resins and finally micro-precipitated through membrane filters with $BaSO_4$, according to the procedure by Pérez-Moreno et al. [36]. The filters were measured by two detector systems, Alpha Analyst™ with passivated implanted planar silicon detectors (Canberra, USA), and Alpha Ensemble® with ion implanted silicon charged particle detectors (ORTEC, USA) for 24 h or more.

## 3.7 Assessment of contamination

To put the concentration of potential toxic elements in context, a risk assessment tool was used to determine the degree of contamination at the mining sites. This diagnostic tool uses the concentration of eight substances: Hg, Cd, Pb, As, Cr, Cu, Zn and polychlorinated biphenyl (PCB) in the top 1 cm layer of lake sediment [37]. It compares the concentrations with average values taken from 50 lakes from Europe and America and assesses the degree of contamination from low to very high

$$C_d = \sum_{i=1}^{8} C_f^i = \sum_{i=1}^{8} \frac{\bar{C}_{0-1}^i}{C_n^i} \qquad (Eq.11)$$

where $\bar{C}_{0-1}^i$ is the average concentration of element $i$ in sediment in the 0-1 cm layer (in ppm) and $C_n^i$ is the standard preindustrial reference level determined from various European and American lakes (in ppm). The ratio, $C_f^i$ represents the contamination factor for that element $i$, and $C_d$ is the degree of contamination, summed for all the calculated $C_f^i$ (substances).

$C_f^i$ values are evaluated by using four risk categories, low if less than 1, moderate between 1 and 3, considerable if between 3 and 6, and very high if larger than 6. Similarly, for $C_d$, a low degree of contamination is considered for values less than 8, moderate if between 8 and 16, considerable between 16 and 32 and very high if larger than 32. Since PCB was not measured in this work only metals detected by XRF analysis were included, thus a modified version of this diagnostic tool is used where $i < 8$.

## 3.8 Statistical analyses

Statistical analyses of the data included test of normality and distribution of data, principal component analysis (PCA) and hierarchical cluster analysis (HCA). The statistical tests in this thesis was performed by the software IBM® SPSS Statistics (version 26).

### 3.8.1 Hierarchical cluster analysis

HCA was used to study how the different pit lakes or parameters would be clustered in regard to their content (elements, radionuclides, pH and SC for pit lakes) or values (for parameters). This is performed by the software through calculations of distances from one pit lake or parameter to the other in a Euclidean space. By choosing a desired threshold distance, clusters of pit lakes or parameters were obtained. Throughout this work the threshold to separate clusters was set to 50%, i.e. a distance of 12.5 in the Euclidean space.

### 3.8.2 Principal component analysis

PCA is a multivariate analysis that reduces the number of initial parameters (e.g. concentration of Na, Mg, K…Pb) to a few components that are linear combinations of the original parameters in such a way that the first principal component (PC) explains most of the variance in the data, followed by the second PC explaining somewhat lower variance and so on. In each component the parameters are listed with loadings (weights) that can be interpreted as correlations to each component; a high loading would thus indicate that the specific parameter is important in explaining the variance of that particular component.

Once the PCs and loadings were obtained, PCA scores were calculated by taking the product sum of the standardized data to the corresponding loadings in each PC. The resulting vectors with PCA scores were then be plotted to visualize how similar or dissimilar the pit lakes are by studying their relative position to each other. This is somewhat similar to the clustering obtained by HCA. Furthermore, the PC loading vectors were also plotted to aid the interpretation on the relative position of pit lakes in the PCA score plot.

Each value included in PCA was standardized, $P_{std}$, through the use of the arithmetic mean and standard deviation of each parameter among all the samples included

$$P_{std} = \frac{P_i - P_{ave}}{\sigma_P} \qquad (Eq.12)$$

where $P_i$ is the value of a parameter from one pit lake, and $P_{ave}$ and $\sigma_P$ are the mean and standard deviation of that parameter, respectively, for all the samples (pit lakes) included.

# 4  Results

From the sampling of pit lakes, it was evident that in some areas of Sweden certain mines were more common than others. This resulted in that the pit lakes included in the two data sets, north and south, did not contain the same type of mines.

Altogether, data from 39 mining sites were studied, where pit lakes in Northern Sweden were mostly former Cu and Zn mines with relatively young age, whereas pit lakes in Southern Sweden were a mixture of different quarries and Fe mines with a longer history. Thus, the pit lakes were divided into two groups with a geographical separation that is similar to the border outlined by limes norrlandicus [38] and the Illies ecoregion 14 [39] that depict the difference in animal and plant species in Sweden. Furthermore, several pit lakes studied in Northern Sweden had been or were limed annually to maintain a neutral pH. Since liming greatly affects the water chemistry it was an additional reason to study northern lakes separately.

## 4.1 Methodology and quality assurance (paper I)

### 4.1.1 Significance of yield

The yield of a radiochemical procedure reflects the robustness of the procedure, where a high yield would increase the count rate from the sample and thus reduces counting uncertainty and the minimum detectable activity, MDA. However, having a high radiochemical yield but a poor resolution in the spectra can be of little use. Thorium spectra are particularly sensitive to resolution since the $^{229}$Th and $^{230}$Th peaks are close to each other, because of alpha particles with energies 4814 keV and 4687 keV, respectively. The full-width-at-half-maximum, FWHM, of peaks in alpha spectrometry by electrodeposition was around 60 - 80 keV, resulting in small margins for a worsening in resolution (or peak broadening).

The radiochemical yield of Th was on average 47% (paper **I**) indicating that about half of the activity was lost throughout the radiochemical procedure. At the later stages of this work, micro-coprecipitation with $CeF_3$, according to the source preparation Eichrom procedure SPA01 [40], was tested for twelve surface water samples from pit lakes. The average yield of Th was $87\% \pm 10\%$, however, the disadvantage seen was broadening of peaks, as demonstrated in Figure 2.
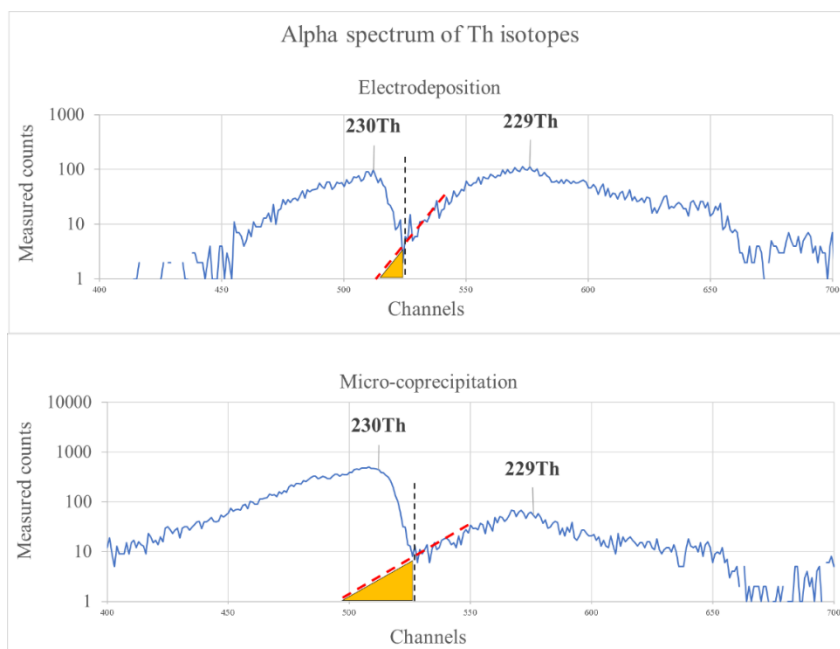
Figure 2 Comparison between alpha spectra from two different water samples prepared either by electrodeposition (top) or micro-coprecipitation (bottom). The black line indicates the beginning of the peak area for [229]Th and the end of the [230]Th area. Due to the peak widths, the resulting loss of counts, or error in the calculated peak area, is indicated by the orange triangle drawn along the red line, which is the assumed decline of the [229]Th peak. The broader the peak, the more flattened is the slope and thus the triangle area becomes larger

## 4.1.2 Optimal analytical technique

In Figure 3 (paper **I**), analysis of [238]U by alpha spectrometry and ICP-MS was compared and were in good agreement. This comparison was made possible through the usage of the conversion factor of 12.35 Bq kg$^{-1}$ ppm$^{-1}$ which is obtained through the calculation taken into account the abundance, half-life and molar mass of [238]U. The uncertainties in Figure 3 are the error propagated uncertainty of alpha spectrometry results and a fix uncertainty of 20% for ICP-MS results, which was assumed to be a reasonable upper limit for the semi-quantitative analysis.

The agreement between the two detection techniques was better in the medium-high activity concentration range, while it was moderate or poor for lower activity concentrations. There could be several reasons for this disagreement.

One is the difference in filtration of the water samples, where ICP-MS required filtration with a filter paper (35-40 µm), while water samples analyzed by alpha spectrometry were in most cases not filtered. Another reason for the difference is the difficulty in selecting the peak area, especially in alpha spectrometry for low activity concentrations or bad resolution. For low activity concentrations (few registered counts) the decision to include or exclude a few counts can have a large impact on the calculation of activity concentration.

The comparison between alpha and gamma spectrometry for surface sediment samples showed that alpha spectrometry is preferable to analyze disequilibrium in the decay chains. It is an optimal analysis for the $^{235,238}$U and $^{232}$Th decay chains, since the first and last radionuclide in the chain is an alpha emitter. Furthermore, alpha spectrometry has a higher sensitivity with detection limit of around 0.5 Bq/kg for sediment (and rock) samples and around 0.5 mBq/kg for water samples. For gamma spectrometry, the main advantage is the higher sample throughput and larger sample mass that can be used. The sensitivity is much lower and uncertainties can be much higher than in alpha spectrometry leading to difficulties in observing a possible disequilibrium. However, for rock samples collected around the pit lakes, secular equilibrium was observed (paper **II**) and these samples can thus be readily analyzed with gamma spectrometry. Saïdou et al. compared the two techniques for twenty soil samples and came to similar conclusions that gamma spectrometry is a valid alternative for samples with a secular equilibrium among the progeny. They found no statistical significance between the results obtained from alpha and gamma spectrometry for $^{238}$U and to some extent also the $^{232}$Th decay series [41].

Furthermore, the activity measured by gamma spectrometry, assuming that proper transmission and coincidence corrections were done, results in the total activity, whereas for alpha spectrometry the activity level corresponds to either a leached or digested sample where varying losses can have occurred. In general, for screening purposes such as identifying areas with higher activity concentration of $^{40}$K, $^{238}$U and $^{232}$Th, gamma spectrometry may be the optimal analytical technique.

An important aspect in the analytical method of choice in environmental sampling is the amount of sample analyzed. The trend is to use lower sample mass when the analytical technique becomes more sensitive. Inhomogeneous radionuclide distributions present in environmental samples (Figure 11 and 12 in paper **II**) can then cause erroneous results if the sample is not-representative for the environment studied. For example, the weight of dry sediments used in gamma spectrometry was about 60 g, while only 1 g for alpha spectrometry.

Thus, although gamma spectrometry can have the highest detection limit compared to XRF, ICP-MS, and alpha and beta spectrometry, it is still preferred due to its robustness and the relatively larger sample mass used in the analysis.

## 4.2 Pit lakes in Southern Sweden (paper II)

In paper **II**, 23 mining sites were included from Skåne to Southern Uppland. Most sites had one main water body and some sites had smaller pit lakes in close proximity, and then they were also sampled. These lakes were sampled in 2015, the majority in April. The majority of the pit lakes are located in Västmanland county and the bedrock for that area is mostly composed by granodiorite, a sub division of granitoid, Figure 3 from SGU [42]. Among the 34 water samples collected, 30 are included in this subchapter, where 10B, 10C, 12B and 17B were excluded since they were not water sample from the pit lake directly.
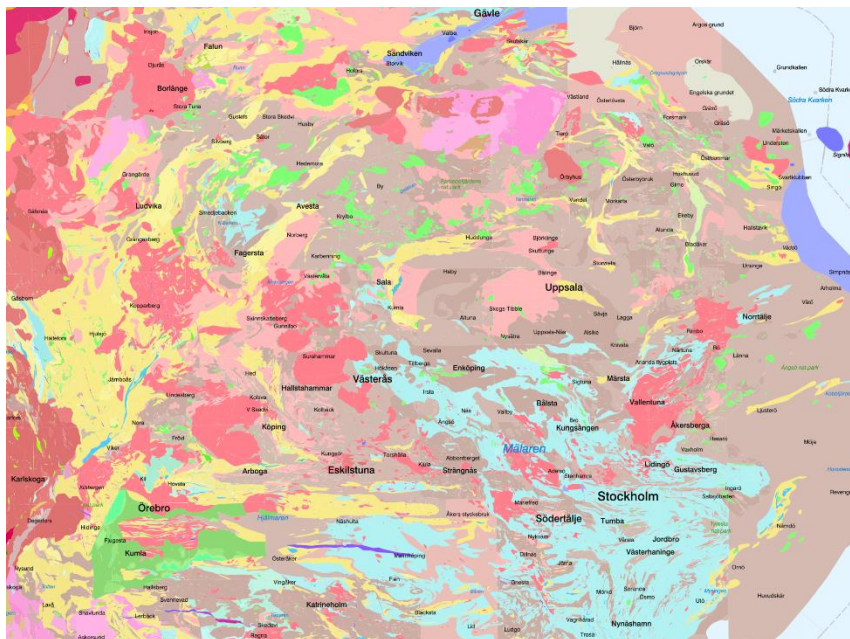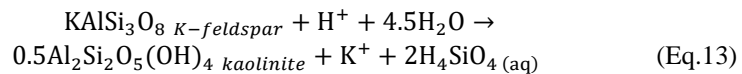


Figure 3 Map of bedrock in the area including the majority of the studied mining sites in Southern Sweden. The main bedrock is composed of granodiorite (light brown) and tonalite (dark brown), granite (light red) and syenitoid (dark red), greywacke (turquoise), rhyolite and dacite (yellow). The bedrock map is from SGU [42] and topographical map from GSD-Vägkartan, ©Lantmäteriet

## 4.2.1 Water quality parameters

pH values in surface water ranged from 4.9-8.4 and generally the limestone quarries had the highest pH values, followed by stone quarries such as granite, and lowest pH was found among metal mines. The lowest pH (4.9) was measured in a pit lake from a former silver mine operated during the years 1483-1900 with an excavated depth of 240 m.

The majority of pit lakes had neutral pH and this could be due to the relatively low amount of pyrite bearing rocks and the abundance of feldspar minerals at these areas. Feldspar is a common component in granitoids and supplies base cations that consume hydrogen ions, which is seen in the chemical reaction below for K-feldspar [43, 44]

$$KAlSi_3O_{8\ K-feldspar} + H^+ + 4.5H_2O \rightarrow$$
$$0.5Al_2Si_2O_5(OH)_{4\ kaolinite} + K^+ + 2H_4SiO_{4\ (aq)} \quad\quad (Eq.13)$$

The specific conductance (SC) in surface water ranged from 47 to 600 µS/cm and there was no clear trend when comparing with the type of mining site. For instance, one of the lowest SC levels, 100 µS/cm, was found in a stone quarry close to Stockholm, and 70 km to the West was another stone quarry with one of the highest SC of 580 µS/cm. Both mines are situated on granitic bedrock. Generally, fresh water have SC levels of 10-1000 µS/cm [45]. However, the water input source can affect SC among other parameters, where water input may be from rain and surface water runoff or from deep groundwater. Groundwater passing through cracks in the bedrock can flush away and dissolve loosely bound ions that will give higher SC levels. This process is largely dependent on the type of bedrock, where e.g. groundwater passing through limestone is known to have high SC levels. On the other hand, granite, due to its hardness, is less affected by weathering and SC levels is likely to be lower. Average SC levels in groundwater in Sweden has been reported to be 750 µS/cm [25] and in rainwater 30-40 µS/cm [46]. Pit lakes, which are in direct contact with the atmosphere and subsequently precipitation, most likely contain a mixture of rain- and groundwater, especially regarding the surface water of the pit lake. Therefore, it can be assumed that pit lakes may have SC levels between 30 and 750 µS/cm.

Two natural lakes were sampled for comparison, located in Katrineholm and Kungälv. The measured pH values were 9.4 and 4.9, respectively. The SC values were 118 µS/cm and 51 µS/cm, respectively, where average SC levels in Swedish lakes are 20-200 µS/cm [47]. A 150 m deep underground silver mine with water filled galleries were also studied in this work, where the water from the largest accessible gallery had a surface temperature of 2.6 °C, pH 8 and SC of 950 µS/cm.

Dissolved oxygen (DO) in surface water ranged from 7.8 mg/L to 12 mg/L, indicating well oxygenated water, which is to be expected since surface water is usually saturated with atmospheric oxygen. The lowest value was found in an Fe mine where the water temperature was 7.3 °C, and at this temperature the oxygen saturation should be around 12 mg/L [25]. This rather low value could be due to the Fe consuming the oxygen by oxidation, reducing the dissolved oxygen in the surface water.

## 4.2.2 Surface water

$^{234,238}$U and $^{210}$Po were detected in all 30 pit lakes whereas $^{230}$Th and $^{232}$Th were detected in 26 and 24 pit lakes, respectively, when using water samples of 0.5 kg. If 1 kg samples were used instead, then Th isotopes would be more frequently detected and the overall counting uncertainties for all radionuclides could also be reduced. The highest $^{234}$U activity concentration measured in surface water was found in a granite quarry with 1700 mBq/kg. This site also had the highest activity concentration of $^{238}$U (1200 mBq/kg), $^{230}$Th (26 mBq/kg), $^{210}$Po (94 mBq/kg) and $^{232}$Th (8.8 mBq/kg). The second highest activity concentration for these radionuclides did not coincide at the same site. For example, the second highest $^{210}$Po activity concentration (55 mBq/kg) was found in a diabase quarry, but with much lower concentrations of $^{238}$U and $^{234}$U: 15 mBq/kg and 16 mBq/kg, respectively.

Altogether, ten pit lakes (eight in south and two in north of Sweden) were analyzed for $^{226}$Ra and $^{210}$Pb, the results are seen in Table 1. The activity concentrations were 2.9 - 77 mBq/kg for $^{226}$Ra, and 2.5 - 27 mBq/kg for $^{210}$Pb. For these lakes, CV of $^{238}$U concentration (1.4) was higher than that of $^{226}$Ra (1.0) and $^{210}$Pb concentrations (0.74).

Table 1 Activity concentration of $^{226}$Ra and $^{210}$Pb in surface water for ten pit lakes, eight in the south and two in the north of Sweden. Results are obtained by alpha spectrometry, $^{210}$Pb is measured by ingrowth of progeny $^{210}$Po. Uncertainties are given for K=1. NM indicates that the radionuclide was not measured

| Pit lake | $^{226}$Ra [mBq/kg] | $^{210}$Pb [mBq/kg] |
|----------|---------------------|---------------------|
| S2A | 18.4 ± 1.1 | 6.6 ± 0.6 |
| S3A | 77.0 ± 3.2 | 13.4 ± 0.7 |
| S4A | 14.5 ± 0.9 | 9.8 ± 0.8 |
| S9 | 7.3 ± 0.3 | 7.1 ± 0.6 |
| S11A | 9.5 ± 0.6 | 2.5 ± 0.2 |
| S14 | 27.5 ±1.7 | 27.2 ± 2.5 |
| S15A | 31.3 ± 1.7 | 5.6 ± 0.4 |
| S16 | 7.7 ± 0.8 | 10.1 ± 0.7 |
| N13A | 2.9 ± 0.1 | 3.6 ± 0.3 |
| N16 | NM | 8.4 ± 0.8 |

## 4.2.3 Surface sediment

Generally, the element concentrations found in surface sediment were a factor of 100 to 1000 times higher than that in surface water. The type of ore mined at the sites was reflected in the element concentrations found in the sediment samples. For example, the silver mine with minerals such as pyrite and galena, PbS, had the highest concentration of lead and sulfur in the sediment. The iron mines had the highest concentrations of Fe in the sediment, and a feldspar (containing aluminum silicates) mine showed the highest concentrations of Al and Si in the sediments. Thus, surface sediments at these pit lakes are mostly minerogenic, i.e. composed of crushed minerals (rocks).

The loss due to calcination, required as part of the sample preparation for XRF analysis, were on average 10 % (range 1 – 42 %) at temperatures of about 1000 °C. Apart from the two sediments with high losses, 30 % and 42 %, sampled from limestone quarries with high carbonate content, the remaining sediments showed a loss of about 4 %. This value is relatively low for lake sediments and for such high temperatures, indicating low organic content. As a comparison, Heiri et al. conducted a laboratory exercise on the loss due to ignition for sediment samples, demonstrating an average loss in sediments with high organic content of about 30 % at 550 °C; in a sediment sample with high carbonate content, the loss was only high (average 36 %) for temperatures of 950 °C [48].

The highest activity concentration of naturally occurring radionuclides measured by gamma spectrometry in surface sediments, were found in a feldspar and a granite quarry. The distribution of $^{238}$U and $^{232}$Th were slightly different in these two quarries. The feldspar quarry had about 1470 Bq/kg of $^{234}$Th (in equilibrium with $^{238}$U), 1400 Bq/kg of $^{40}$K and 170 Bq/kg of $^{232}$Th. While the granite quarry had about 1070 Bq/kg of $^{234}$Th, 1160 Bq/kg of $^{40}$K and the highest measured activity concentration of $^{232}$Th among all the sediment samples, 538 Bq/kg (Table 5 paper **II**). In general, relatively high activity concentrations of $^{238}$U and $^{232}$Th coincided with higher activity concentrations of $^{40}$K, however the opposite was not always true. For example, in a stone quarry the activity concentration of both $^{238}$U and $^{232}$Th were about 70 Bq/kg while $^{40}$K was 970 Bq/kg.

## 4.3 Pit lakes in Northern Sweden (paper **III**)

In paper **III**, 17 mining sites were included from Northern Uppland to Lappland, sampled during October 2015. Most sites had one main water body and some sites had smaller pit lakes in close proximity, and then they were also sampled. The majority of the pit lakes are located in the counties Västerbotten and Lappland, and the bedrock for that area is seen in Figure 4, from SGU [42]. The largest difference in the bedrock composition compared with that in Southern Sweden (Figure 3) is the higher occurrence of granite and greywacke and less of content granodiorite and tonalite. In general, the pit lakes in Northern Sweden were larger compared to those in the south, and therefore for one pit lake (site N2) with a surface area of 0.03 km$^2$, two surface water samples were collected at opposite shores along the longest dimension of the lake (330 m). Other differences between the pit lakes in papers **III** and **II** are that most of the northern pit lakes were former metal mines, mainly for Cu and Zn. Also, the oldest recorded mine among the northern pit lakes is from 1924 and the most recently used mine closed in 2001. Thus they are relatively young, while some pit lakes in paper **II** date back as far as the 19$^{th}$ century.

Among the 27 water samples collected, 21 are presented here, where 9A, 9B, 10A, 10C and 11B were excluded, similarly for the sediment samples from these sites. Although these were some form of pit lakes, it is not known with certainty if resulted after mining activities and naturally filled with groundwater, as described in the introduction.
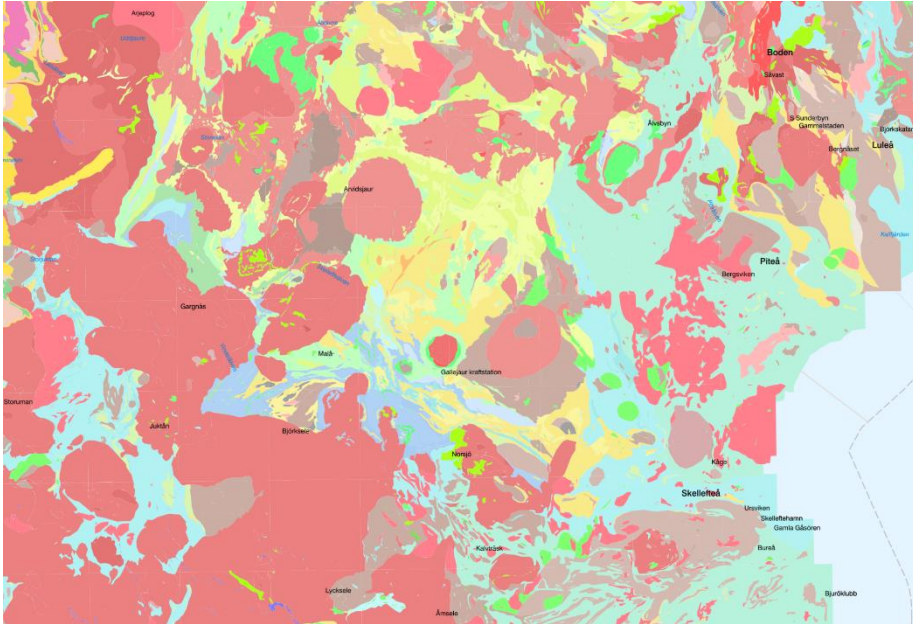
Figure 4 Map of bedrock composition shown for the area including the majority of the mining sites in Northern Sweden. The main bedrock is composed of granite (dark red), greywacke (turquoise) and rhyolite and dacite (yellow). Bedrock map is from SGU [42] and topographical map from GSD-Vägkartan, ©Lantmäteriet.

## 4.3.1 Water quality parameters

From what is known, eight sites in paper **III** are being limed annually and are included in a monitoring program: Two of these sites have two pit lakes a few meters apart and it was assumed that both are being limed, resulting in 10 limed pit lakes in total. It is not known if U is included among the monitored elements. U exists practically as carbonate complexes, $UO_2(CO_3)_3^{4-}$, in neutral and alkaline water, which increases its solubility [7, 18, 49]. For example, calcium carbonates added as corrosion control has been seen to form carbonate complexes with U in the soil, causing an in-situ leaching and contamination of underlying groundwater [50].

pH values in surface water ranged from 5.7 to 9.3. pH values around 9 were found at three different mining sites. Two of these sites are a former Cu and Au mine and a Zn mine, where both pit lakes are limed annually. The third is a Pb and Zn mine with, to our knowledge, no information on liming, but a pH of 9.3 strongly indicates that liming has been made. The pit lake with pH 5.7 has been studied previously and trials have been conducted to improve the water quality by liming to reduce metal concentrations by precipitation [12].

The specific conductance (SC) in surface water were 3 - 190 mS/m with an average of 60 mS/m. As a comparison, the pit lakes in Southern Sweden had an average SC of 26 mS/m (5 - 60 mS/m), indicating that SC increase after addition of lime, as previously reported [12, 51, 52]. The highest SC was found in a sulfide bearing mine containing the metals Fe, Zn, Cu, Pb and As. The mine was operated between 1970 and 1991 and the pit was covered with till after mine closure [53]. This pit lake had during the sampling in 2015 a pH of 7.2 and SC of 190 mS/m. Earlier measurements performed by Ramstedt et al. during 1998 measured pH to 4.8 and SC about 107 mS/m in the surface [54], and it is clear that the liming conducted has improved the pH and increased the SC.

Similarly, in another pit lake sampled during 2015 the pH was 9.0 and SC 170 mS/m, while earlier measurements by Lu et al. between 2001 and 2004 showed low pH (approximately 3) and SC (approximately 150 mS/m) before liming and addition of sewage sludge. After this treatment, pH increased to about 6.4 and SC to 190 mS/m in 2004 [12]. As a comparison to the pH and SC values in pit lakes, a study on 59 forest lakes in Northern Sweden (latitudes 59°30′N to 68°15′N), performed by Borg in 1987 showed an average SC of 3 mS/m (range 1.5 - 6 mS/m) and an average pH of 6.8 (range 5.7 - 8.8) [55].

## 4.3.2 Surface water

The activity concentration of $^{234,238}$U was much lower in Northern than in Southern Sweden. The average activity concentration of $^{238}$U among the 21 pit lakes was 12 mBq/kg (2.0), whereas for southern pit lakes the average was 180 mBq/kg (1.6) where CV is given in parenthesis. Despite that most studied pit lakes in Northern Sweden were a former Cu or Zn mine, the activity concentration of $^{238}$U varied much more compared to the southern pit lakes, which included different kinds of quarries and mines. Furthermore, the ratio of $^{234}$U to $^{238}$U in surface water ranged between 0.7 to 2.3 where the highest was found in a non-limed Cu and Zn mine.

The activity concentration of $^{230,232}$Th and $^{210}$Po was also lower, with average activity concentrations of about three times lower than in Southern Sweden. The highest activity concentration of $^{234,238}$U was found in a former gold mine operated from 1989 to 2001. This pit lake also had the highest concentration of As in surface water and surface sediment, 33 µg/L and 160 ppm, respectively. Arsenic is an element known to occur in gold deposits [56]. There is no record of this pit lake being limed, but it is included in a monitoring program.

The highest activity concentration of $^{210}$Po, 16 mBq/kg, was found in a former Cu and Au mine, and no other element was found in elevated concentrations at this site.

### 4.3.3 Surface sediment

When comparing 15 surface sediment samples, the concentration of elements varied relatively little among the northern pit lakes (compared to southern pit lakes): CV ranged from 0.09 for Si to 1.4 for Cu. This is most likely due to the similarities among the mines included, being mainly Cu and Zn mines. Relatively low CV compared to southern pit lakes could also be seen for the radionuclides, $^{234}$Th (0.5 for northern, 1.8 for southern pit lakes) and $^{232}$Th (0.4 for northern, 0.9 for southern pit lakes). However, CV for $^{40}$K (0.3 for northern, 0.4 for southern pit lakes) indicates that the activity concentration is more evenly spread in surface sediments (or bedrock) among the studied sites across Sweden compared to $^{238}$U and $^{232}$Th. The average loss due to calcination was 4% with range 1 - 9%, indicating low amounts of organic matter in the surface sediment and also low variation among the pit lakes.

Compared with the southern pit lakes, the average S, Fe, Zn, Ba and Pb concentrations were at least twice as high in the northern pit lakes, while the U concentration was on average half of those found in southern pit lakes. The highest activity concentration of $^{234}$Th in surface sediments was found in the same Au mine where the highest activity concentration of $^{234,238}$U in surface water was found. Similarly, the lowest activity concentration of $^{234}$Th in surface sediments was found in the pit lake with one of the lowest activity concentrations of $^{234,238}$U in surface water. At both these sites, the ambient dose equivalent rate was 0.08 µSv/h.

## 4.4 ICP-MS results (Papers II, III)

Table 2 summarizes the concentration of elements measured by ICP-MS in surface water from the pit lakes in Southern and Northern Sweden included in the previous subchapters. The table also includes the three natural lakes sampled in this work and also results from 59 forest lakes in Northern Sweden by Borg [55] for comparison.

### 4.4.1 Southern Sweden

One thing in common among the 23 mining sites is that the most common elements found in Earth's crust show little variation from site to site. It is instead elements such as Mn, Zn and Pb that showed the largest variations. The elemental concentration in surface water does not necessary reflect the concentration in the lake as a whole, but rather reflect the solubility or adsorption to soluble particles (colloids). For instance, the highest Fe concentration in surface water, 5.5 mg/L, was found in a diabase quarry, an ore containing up to 14% Fe, [57]. In contrast, at a former iron mine extracting the ore skarn, which contains up to 23 % Fe [58], the concentration of Fe in surface water was below detection limit, which is about 100 ng/L. Fe solubility and mobility largely depend on the Fe oxidation state, where Fe(III) is less mobile than Fe(II). Fe can also adsorb to microorganisms and suspended colloids, further increasing its concentration in surface water.

The highest concentration of Pb in surface water, 690 µg/L, was found in a former silver mine, also containing pyrite. As a comparison, the threshold for Pb in suitable drinking water in Sweden is 10 µg/L [59]. Common elements found in silver containing rocks are S, Zn, As and Pb [60]. The concentration of Zn in this former silver mine was also the highest among the included pit lakes (5870 µg/L). However, S and As did not show similar enhancement, 74 µg/L and below detection limit, respectively. This lake also had a pH of 4.9 which further explains the high concentration of Zn and Pb, since low pH generally increases metal solubility and mobility [61]. Therefore, it is likely that the oxidation of pyrite and sulfide minerals both caused acidic water and high concentrations of Zn and Pb.

Table 2 Summary of the concentration of elements in surface water from 30 pit lakes in Southern Sweden and 21 in Northern Sweden. The range is given together with the coefficient of variation (CV). Natural lakes are shown for comparison, sampled in Katrineholm, Kungälv and Gävle, also results from 59 forest lakes in Northern Sweden by Borg in 1987. ND indicates that the element was not detected and NM indicates that the element was not measured

|  | Na [mg/L] | Mg [mg/L] | P [mg/L] | Al [mg/L] | Si [mg/L] | S [mg/L] |
|---|---|---|---|---|---|---|
| **South:** Range | 0.03-130 | 0.1-100 | ND-9 | 0.8-60 | 7.7-380 | ND-640 |
| (CV) | (1.2) | (1.0) | (0.8) | (1.2) | (0.9) | (0.6) |
| **North:** Range | ND-26 | ND-194 | ND-6 | ND-10 | NM | ND-5880 |
| (CV) | (0.6) | (1.7) | (0.9) | (0.8) |  | (1.1) |
| **Borg** [55] | - | - | - | 0.010-0.2 | - | - |
| **Natural lakes** |  |  |  |  |  |  |
| Katrineholm | 15 | 9 | 1 | 9 | 180 | 114 |
| Kungälv. | 12 | 2 | ND | 5 | NM | ND |
| Gävle | 50 | 6 | ND | 9 | NM | 161 |

|  | K [mg/L] | Ca [mg/L] | Cr [µg/L] | Mn [µg/L] | Fe [mg/L] | Cu [µg/L] |
|---|---|---|---|---|---|---|
| **South:** Range | 1-45 | 8-380 | ND-20 | 0.5-510 | ND-6 | ND-70 |
| (CV) | (0.6) | (0.7) | (1.4) | (2.0) | (1.4) | (0.9) |
| **North:** Range | ND-67 | 2-1260 | ND-20 | ND-1050 | ND-0.6 | ND-130 |
| (CV) | (1.0) | (1.2) | (0.7) | (1.8) | (0.9) | (1.4) |
| **Borg** [55] | - | - | <0.1-0.6 | 1-88 | 0.010-1.5 | 0.1-2 |
| **Natural lakes** |  |  |  |  |  |  |
| Katrineholm | 14 | 63 | 3 | 50 | 0.7 | 10 |
| Kungälv | 9 | 21 | 2 | 80 | 0.2 | 6 |
| Gävle | 7 | 54 | 4 | 21 | 2 | 5 |

|  | Zn [µg/L] | As [µg/L] | Sr [µg/L] | Ba [µg/L] | Pb [µg/L] | U [µg/L] |
|---|---|---|---|---|---|---|
| **South:** Range | ND-5870 | ND-4 | 37-310 | 3-200 | 3-690 | 0.1-110 |
| (CV) | (1.7) | (0.7) | (0.6) | (1.5) | (3.1) | (1.6) |
| **North:** Range | ND-3900 | ND-32 | 3-610 | ND-260 | ND-80 | ND-4.1 |
| (CV) | (1.2) | (2.3) | (0.9) | (2.3) | (1.8) | (1.2) |
| **Borg** [55] | <0.4-8.5 | 0.06-1.2 | - | - | 0.1-0.8 | - |
| **Natural lakes** |  |  |  |  |  |  |
| Katrineholm | 340 | ND | 70 | 17 | 16 | 0.2 |
| Kungälv | 780 | ND | 10 | 2 | 4 | ND |
| Gävle | 311 | 0.4 | 40 | 6 | 4 | 0.8 |

## 4.4.2 Northern Sweden

Although most concentrations of elements were within the same range as those in Southern Sweden, the main differences were higher Ca and S concentrations and lower Fe and Pb concentrations, despite several pit lakes in Northern Sweden being sulfide mines with metals such as Fe, Zn, and Pb. This is likely due to the liming activities causing increased pH, and by the addition of Ca also precipitation of Fe hydroxides and other metals co-precipitating with it, which reduces their concentration in the surface water. The high concentration of sulfur is likely in the form of sulfates, since sulfides are generally insoluble. The sulfates are a result of weathering of sulfide bearing rocks, as seen in Eq.1.

One of the largest pit lakes sampled (site N2) had a surface area of 0.03 km$^2$ and a volume of approximately 500,000 m$^3$. Two water samples were collected from this pit lake (during the same day) at opposite sides of the lake to study the horizontal variation. The results are given in Table 3, where the largest relative variation is seen for Mg, K and Ba. This variation includes both the actual horizontal variation found within the lake and the semi-quantitative results of the ICP-MS analysis. In general, most parameters show similar values in the lake surface.

Table 3 Comparison of two water samples taken from one of the largest pit lakes in this work, with a surface area of 0.03 km$^2$ and volume 500,000 m$^3$. The samples were taken from opposite sides of the lake along the longest dimension, 330 m

|        | pH  | SC [mS/cm] | Na [mg/L] | Mg [mg/L] | Al [mg/L] |
|--------|-----|------------|-----------|-----------|-----------|
| WN2A   | 8.2 | 84         | 12        | 12        | 5         |
| WN2B   | 7.8 | 83         | 19        | 20        | 4         |
|        | S [mg/L] | K [mg/L] | Ca [mg/L] | Mn [µg/L] | Cu [µg/L] |
| WN2A   | 2410 | 46      | 500       | 52        | 18        |
| WN2B   | 2400 | 28      | 380       | 40        | 12        |
|        | Zn [µg/L] | Sr [µg/L] | Ba [µg/L] | Pb [µg/L] | U [µg/L] |
| WN2A   | 220  | 310     | 11        | 3.4       | 0.4       |
| WN2B   | 230  | 330     | 7         | 2.4       | 0.4       |

## 4.5 Statistical treatment of data (paper IV)

Hierarchical cluster analysis (HCA) and principal component analysis (PCA) were used on data from pit lakes from both the southern and the northern parts of Sweden. These two analyses provided an overview of the similarities and dissimilarities among the parameters measured. Furthermore, PCA and HCA were also used to study similarities among pit lakes by distinguishing the type of mine they originated from.

### 4.5.1 Principal component analysis

In order to study the pit lakes grouped together around the origin in paper **IV** Figure 3, a separate PCA was performed where Ca and the elements Na, Mg, K and Sr, which were highly correlated with the concentration of Ca (Table 2 paper **IV**), were excluded. This was due to the ambiguity of the correlation between Ca and type of mines. To visualize the reason for excluding these elements, Figure 5 shows the concentration of Ca in surface water for 44 pit lakes (excluding the unknown mines) where they are categorized into five groups, limestone/marble quarries, feldspar/granite/stone quarries, Fe mines, non-limed Cu/Zn/Ag/Au mines, and limed Cu/Zn mines.
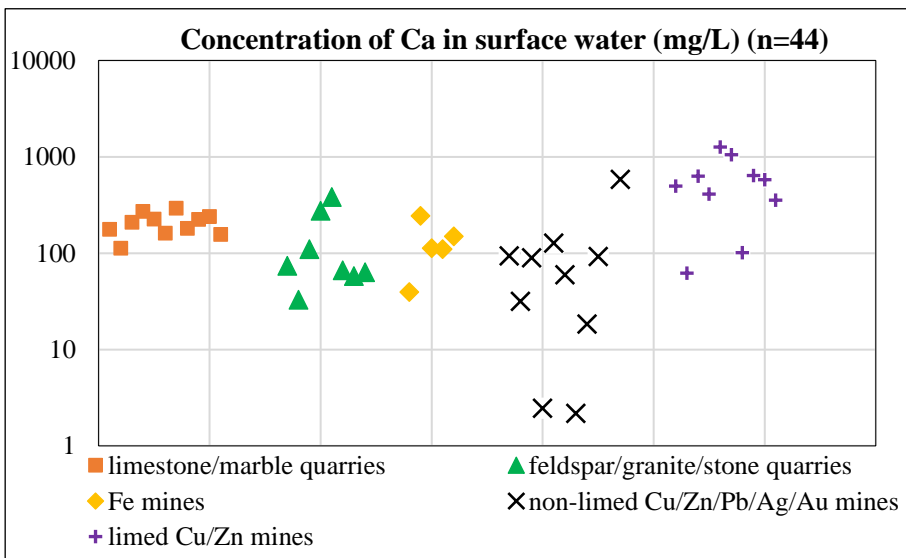


Figure 5 Concentration of Ca in surface water for 44 pit lakes categorized into five groups

The concentration of Ca in surface water is not necessarily high and unique for limestone and marble quarries; limed Cu and Zn mines might even have higher concentration. What can be seen, however, is a much smaller spread in the concentration of Ca in surface water for the limestone and marble quarries, compared to surface water in other mines. Thus, the inclusion of Ca and elements highly correlated with its concentration, can be misleading when trying to characterize different types of mines by PCA through surface water.

The pit lakes that were chosen for a separate PCA (n=27) were those within a radius of 3 from the origin in Figures 3a and 3b in paper **IV,** and the parameters included were pH, and concentration of Mn, Cu, Zn and Pb. In addition, the three natural lakes that were sampled in Katrineholm, Kungälv, and Gävle were included in this analysis for comparison. The PCA was performed in a similar manner as described in paper **IV** and the results are given in Table 4 and Figure 6. The parameters given in Table 4 were those that best explained the variance among these 27 pit lakes; inclusion of any element or radionuclide worsened the total variance explained by the first two PC.

Table 4 Results from PCA after a Varimax rotation for 27 surface water samples from pit lakes in Sweden. Two principal components (PCs) explaining 66% of the total variance is presented. PC1 is highly connected to transitional and post-transition metals and PC2 to pH and Pb.

|  | Rotated components | |
|---|---|---|
|  | **PC1** | **PC2** |
| **pH** | -0.57 | **0.67** |
| **Mn** | **0.74** | -0.20 |
| **Cu** | **0.77** | -0.16 |
| **Zn** | **0.61** | 0.14 |
| **Pb** | 0.07 | **0.94** |
| **Variance explained (%)** | 44 | 22 |
| **Cumulative (%)** | 44 | 66 |
| **Eigenvalue** | 2.2 | 1.1 |

The PC1-PC2 plot in Figure 6 shows that most of the pit lakes are still found centered around the origin. The difference is very small despite excluding several pit lakes and parameters that were previously used in Figure 3 in paper **IV**. In this analysis, only two pit lakes were explained (or characterized) by the PC: the Pb mine in the lower right and a Zn mine in the top left, which correspond to the Pb and Zn loadings, respectively.

It seems that about half of the pit lakes cannot be well explained by the obtained PC based on the studied parameters in this work and for the samples collected (surface water). However, the largest difference between Figure 6 below, and Figure 3 in paper **IV** is the loadings of Cu, Zn and Pb, which were seen to be closely grouped in the latter figure, whereas in Figure 6, Pb and Zn are clearly separated. Thus, it would be reasonable to perform two PCAs on similar data sets, one separate for major elements (Na, Mg, K, Ca etc.) and one for trace elements (Mn, Cu, Zn, Pb etc.), which in principle corresponds to PCA analyses on each chemical group, alkali and alkaline earth metals, transitional and post-transition metals (and radionuclides).
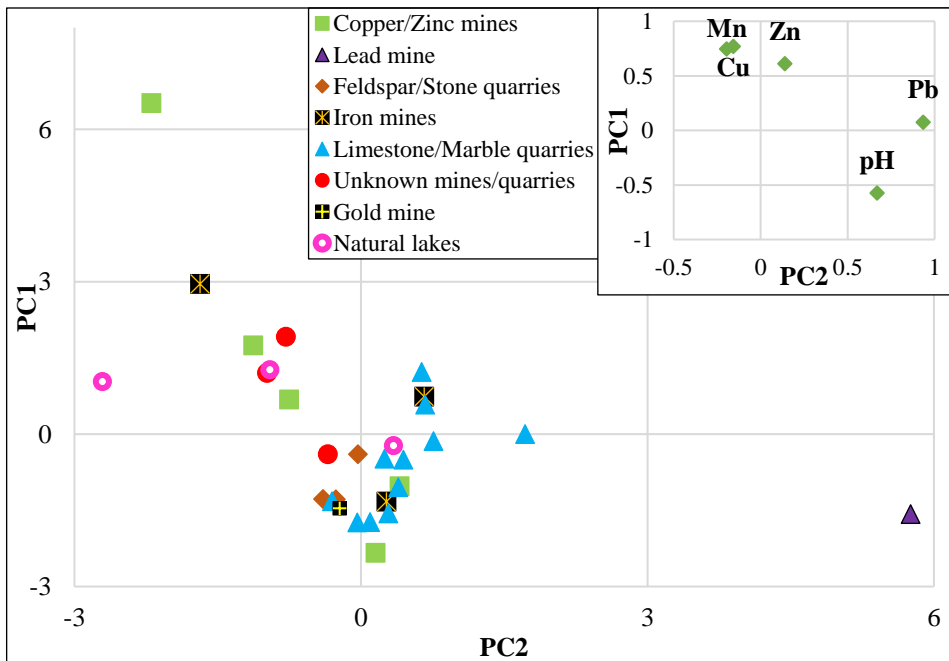


Figure 6 Plots of PCA score and loading for 27 surface water samples from pit lakes in Sweden, which were seen to be grouped around the origin in paper **IV**, Figure 3a and 3b. The present PCA focused on the trace elements Mn, Cu, Zn and Pb in order to study the position of pit lakes relative to each other, without the inclusion of Ca and elements highly correlated with the Ca concentration

## 4.6 Vertical distributions (paper V)

From the survey of pit lakes across Sweden (papers **II, III**), where mainly surface water was sampled, only few sites could be identified which contained higher concentration of naturally occurring radionuclides. One of these sites was found in the municipality of Köping, and is a former feldspar mine in operation between 1890 and 1980, with a maximum excavation depth of 110 m [62].

The bathymetric data showed a maximum depth of 60 m, which was found in a relatively small area close to the center of the pit lake (Figure 1 in paper **V**). The depth reading on the sonar quickly changed to about 50 m if the boat deviated slightly in position due to the rocky and non-flat bottom of the pit lake. This caused difficulties in using the Niskin bottle at the deepest part, and therefore the maximum sampled depth was 50 m. Furthermore, it was found useful to have a sonar with high resolution since the measuring tape connected to the sampling equipment to determine depth of sampling, could be verified by observing the sampling equipment on the display of the sonar at each depth.

The surface area of the pit lake was about 0.01 km$^2$ and the relative depth, $D_r$ (Eq.3), was calculated to 49%, which is much higher than for natural lakes, e.g. lake Vänern in Sweden has a $D_r$ of 0.12% [11].

### 4.6.1 Water quality parameters

Temperature (T), pH, SC, ORP and DO were measured along the 50 m depth in 1-2 m incremental steps. The quoted uncertainties of these parameters from the manufacturer are as follows, $\pm$ 0.1 °C (T), $\pm$ 0.2 (pH), $\pm$ 0.5% (SC), $\pm$ 20 mV (ORP) and $\pm$ 0.1 mg/l (DO) [63]. Several observations were made from the vertical distribution of these parameters, shown in Figure 7, redrawn from paper **V** (Figure 3).

The readings of pH, SC and ORP are relatively stable in the top 30 m layer of the water, only T and DO are seen to decrease from surface water to about 15 m depth and then remain stable down to 30 m depth. The increase of temperature from 15 m up to the surface water is most likely due to absorption of sun rays. DO being saturated in surface water is seen to decrease slowly in the top 15 m layer which could be due organisms in the surface water consuming the oxygen and due to the limited vertical mixing of atmospheric oxygen with depth. Collectively, the parameters show relatively well mixed water layer in the top 30 m.
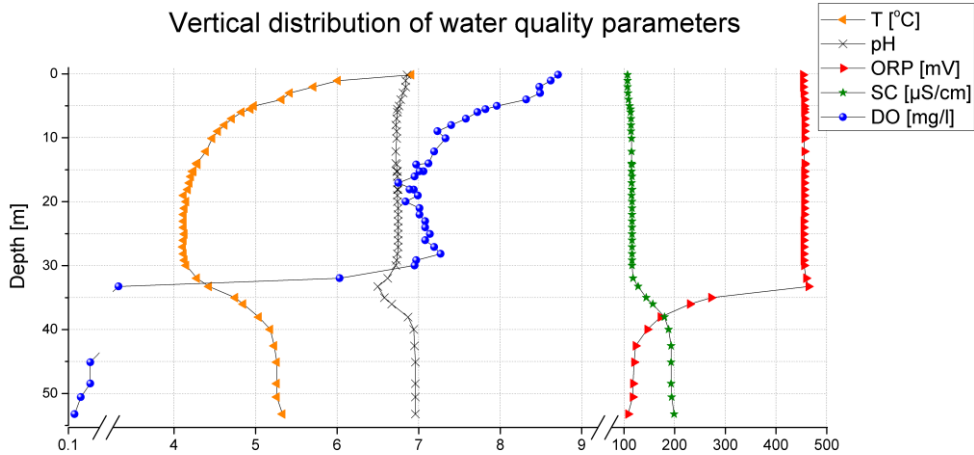
Figure 7 Vertical distribution of temperature (T), pH, ORP, SC and DO along the depth of the pit lake. Note the breaks of the horizontal axis

The shapes of the profiles are similar to what has been observed in other studies in lakes with similar depth, both in acidic pit lakes [12, 64, 65], and in neutral volcanic lakes [66], with SC being relatively constant to about 30 m depth and inversely proportional to ORP, and ORP following the shape of the DO.

The lake showed a clear stratification at around 30 m depth where all parameters exhibit a sharp gradient. This stratification does not have to be permanent. However, since the measurements were made in April, when lakes can undergo a turnover event (mixing of the water), this stratification seems stable enough to withstand the mixing, at least at the time of measurement.

The sharp decrease of DO from 7 mg/L at 30 m depth to practically anoxic levels 10 m further down may be due to two reasons. 1) If the chemical composition of the water is sufficiently different, the lake turnover event would not be strong enough to mix the two water layers. Thus, only the upper layer, which is directly influenced by ambient temperatures and wind forces is mixed, which is indicated by the parameters being practically constant in this layer. Since the vertical mixing of DO is limited to the upper layers of the lake, this would create a sharp gradient where the two water layers meet. 2) Another reason could be a layer of microbial activities at 30 m depth, depleting oxygen through oxidation processes and by decomposing organic matter.

The ORP reading of 450 mV and the aerated water in the top 30 m water layer would indicate oxidizing conditions, where Fe(II) would oxidize to Fe(III) leading to Fe-(co)precipitation which can efficiently scavenge ions in solution. The sharp decrease of DO at 30 m depth would then cause a reduction in ORP, shifting to more reducing conditions (100 mV). This would in turn reduce the Fe(III) (precipitate) to Fe(II) causing it to re-dissolve in the water, releasing any adsorbed ions, which thus leads to an increase in SC, as observed.

## 4.6.2 Stable elements

The vertical distribution of the concentration of elements in surface water can be seen in Figure 7 redrawn from paper **V**, where a) shows the alkali and alkaline earth metals and b) the transitional and post-transition metals. The samples were collected at 0 m (surface), 10, 20, 25, 30, 35, 40, and 50 m depth. Among the presented elements, the concentration of Mg (8%) and Na (13%) were found with least variation with depth followed by Ba (25%), Sr (30%), Rb (31%), Al (37%), and Ca (38%), where CV is given in parenthesis.

The maximum concentration of Pb, Y and Zn seem to occur at 20-30 m depth, while Mn and Fe have distinct maxima at 40 m depth. The distinct vertical distributions of Fe and Mn increasing near the bottom has also been seen in other studies [67-69]. One in particular studied two pit lakes (29 and 50 m depth) in Northern Sweden [12] with similar vertical distributions of Fe and Mn, but with different distributions of Al and Ca.
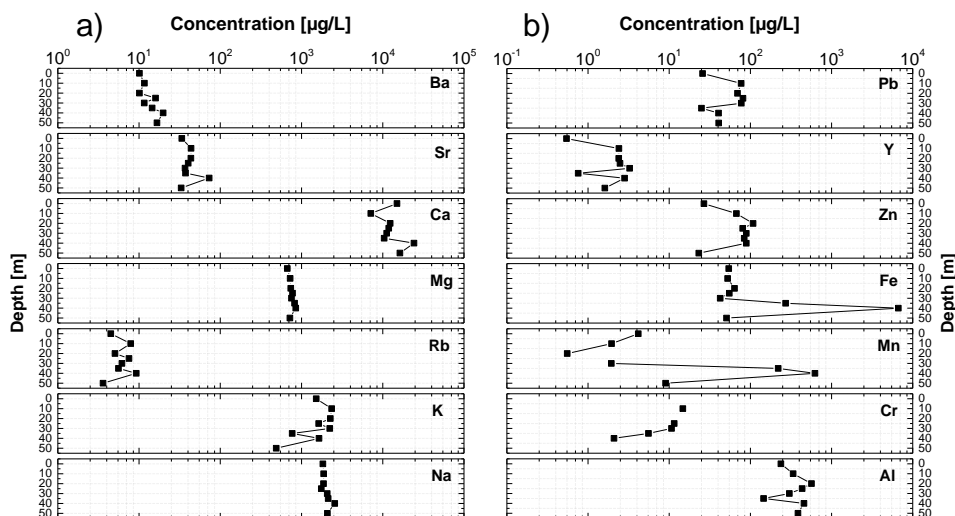


Figure 8 Vertical distributions of elements along the depth (redrawn from paper **V**) where a) shows the alkali and alkaline earth metals and b) the transitional and post-transition metals. The samples were collected at 0 m (surface), 10, 20, 25, 30, 35, 40, and 50 m depth and the concentrations are shown in μg/L.

Achterberg et al. [69] analyzed lake Esthwaite Water (Cumbria, UK) along the 15.5 m depth in June, August and September with vertical distributions of Fe and Mn similar to those obtained here. However, a seasonal variation for Zn was observed in that lake, having similar vertical distribution as Fe and Mn in August but more stable concentration levels with depth in September. This could be due to a turnover event which can occur twice a year for certain lakes, in spring and in fall. This is especially true for shallow lakes where it is more difficult to maintain a permanent stratification. It is interesting to note that the seasonality effects did not affect the vertical distribution of Fe and Mn as it did for Zn. This might indicate that Fe and Mn distributions are more dependent on pH and ORP rather than temperature.

### 4.6.3 Radionuclides

The vertical distribution of $^{226}$Ra, $^{210}$Pb and $^{210}$Po (Figure 4 in paper **V**) showed that activity concentration of $^{226}$Ra was about six times higher than that of $^{210}$Pb and $^{210}$Po. The activity concentration of $^{238}$U and $^{234}$U in surface water in this lake was 179 and 260 mBq/kg, respectively (paper **II**), i.e. about twice as high as $^{226}$Ra. Since these radionuclides all belong to the same decay series, relative differences in activity concentration may be due to differences in chemical behavior, e.g. mobility, solubility and affinity of adsorption to other suspended particles or organisms. In addition, radionuclides liberated from the bedrock could propagate with groundwater through cracks in the bedrock and deposit in the pit lake.

Mn and Fe had similar vertical distribution as $^{226}$Ra, $^{210}$Pb and $^{210}$Po, where the highest concentrations were seen in the anoxic layer (35-50 m depth). This situation was also demonstrated in a study of a 30 m deep fjord where the highest activity concentration of $^{210}$Pb and $^{210}$Po, both particulate and dissolved fraction (<0.2 µm), coincided with the highest concentration of Fe and Mn [68]. In contrast, in a study by Balistrieri et al., a lake with a maximum depth of 32 m was analyzed for $^{210}$Po, $^{210}$Pb and stable Pb throughout the depth [67]. They found that $^{210}$Po and $^{210}$Pb decreased by 52% in the transition from oxic to anoxic conditions, possibly due to sulfur precipitation.

The solubility of divalent metals, such as Ra, Pb and Po, is largely determined by the presence of sulfates, carbonates and chlorides which increase their solubility in that order [70]. Thus, general observations from one aqueous system could differ due to the presence and concentrations of these ligands. In the studied pit lake, the sulfur concentration was not measured at all depths, but was about 25 mg/L at 10 m depth and 9 mg/L at 30 m depth.

Although the vertical distribution of activity concentration differed in magnitude for $^{226}$Ra, $^{210}$Pb and $^{210}$Po, the relative changes with depth were the same (Figure 4 in paper **V**), indicating that their presence in the water is likely due to similar mechanisms or chemical species.

Analyses of relative activity concentration can also help to identify any input originating from outside the lake, e.g. for $^{210}$Pb. $^{222}$Rn that emanates from the surroundings can dissolve into the surface water and when decaying into $^{210}$Pb, the concentration in surface water would increase. Analyses of relative activity concentration may also be useful when comparing different types of lakes (mines). Therefore, for reference purposes, the ratios of $^{210}$Po to $^{210}$Pb, total Pb to $^{210}$Pb and the ratios of $^{226}$Ra, $^{210}$Pb and $^{210}$Po to Fe are given in Table 5.

Another interesting observation in paper **V** (Figure 4) is the vertical distribution of stable Pb and $^{210}$Pb that are almost inversely proportional to each other, showing that the vertical distributions of isotopes of the same element are not necessarily similar, at least when water samples are only filtered with 35-40 µm pore size filters. Of the studied elements, Y had the most similar vertical distribution as stable Pb.

Table 5 Ratios between activity concentrations for the studied radionuclides $^{226}$Ra, $^{210}$Pb, $^{210}$Po to the (activity) concentration of $^{210}$Pb, total Pb and Fe along the depth of the pit lake. The values in bold correspond to the depth at which the activity concentration of $^{226}$Ra, $^{210}$Pb and $^{210}$Po and concentration of Fe were the highest. Total (stable) Pb had the highest concentration at 25 m depth. The errors show the combined uncertainties (K=1) where 20% uncertainty has been assumed for the concentration of Fe and total Pb

| Lake depth [m] | $\dfrac{^{210}Po\ mBq/kg}{^{210}Pb\ mBq/kg}$ | $\dfrac{^{210}Pb\ mBq/kg}{total\ Pb\ \mu g/l}$ | $\dfrac{^{226}Ra\ mBq/kg}{Fe\ \mu g/l}$ | $\dfrac{^{210}Pb\ mBq/kg}{Fe\ \mu g/l}$ | $\dfrac{^{210}Po\ mBq/kg}{Fe\ \mu g/l}$ |
|---|---|---|---|---|---|
| 0 | $0.83 \pm 0.10$ | $0.52 \pm 0.11$ | $1.42 \pm 0.29$ | $0.25 \pm 0.05$ | $0.20 \pm 0.05$ |
| 10 | $0.96 \pm 0.11$ | $0.14 \pm 0.03$ | $1.43 \pm 0.29$ | $0.21 \pm 0.05$ | $0.20 \pm 0.04$ |
| 20 | $0.99 \pm 0.09$ | $0.18 \pm 0.04$ | $1.28 \pm 0.26$ | $0.20 \pm 0.04$ | $0.19 \pm 0.04$ |
| 25 | $0.93 \pm 0.08$ | $0.16 \pm 0.03$ | $1.51 \pm 0.31$ | $0.24 \pm 0.05$ | $0.22 \pm 0.05$ |
| 30 | $0.79 \pm 0.06$ | $0.22 \pm 0.04$ | $1.88 \pm 0.39$ | $0.40 \pm 0.08$ | $0.31 \pm 0.07$ |
| 35 | $0.89 \pm 0.05$ | $1.74 \pm 0.35$ | $0.69 \pm 0.14$ | $0.16 \pm 0.03$ | $0.14 \pm 0.03$ |
| **40** | $\mathbf{0.84 \pm 0.05}$ | $\mathbf{2.08 \pm 0.42}$ | $\mathbf{0.05 \pm 0.01}$ | $\mathbf{0.013 \pm 0.003}$ | $\mathbf{0.013 \pm 0.002}$ |
| 50 | $0.76 \pm 0.08$ | $0.31 \pm 0.06$ | $1.73 \pm 0.35$ | $0.25 \pm 0.05$ | $0.19 \pm 0.04$ |

# 5 Discussion

## 5.1 Sample preparation

A difference in sample preparation between this work and other studies of lake waters is that water samples were either not filtered or filtered with 35-40 µm filter paper, as opposed to the more common membrane filtration with a pore size of 0.45 µm. Water samples analyzed by alpha spectrometry were in most cases not filtered since the collected water was mostly free from visible debris, while samples analyzed by ICP-MS were always filtered as part of the laboratory procedure. The reason for the much coarser filtration employed in this work was to avoid overlooking pit lakes with relatively high activity concentration of radionuclides, since for neutral pH most elements exist in water as molecules and larger aggregates. Another reason was to increase the knowledge on the activity concentration of naturally occurring radionuclides in what can be considered as raw (35-40 µm filtered) water. The drawback is that comparisons with other studies may not be justified if an element is more likely bound to particles larger than 0.45 µm.

Regarding particle sizes in surface water, Buykx et al. separated varying sizes of clay minerals from water samples through several membrane filters (<0.025 µm to >1.2 µm) and found the composition of Al, Si and Fe to be uniform despite the different sizes [71, 72]. They also showed that for European rivers, Ca, K, Na and Mg are likely bound to particles smaller than 0.2 µm, although Fe and Mn were seen to be associated with larger particles than 0.2 µm. Another interesting conclusion was that differences in the chemical composition of particles in river water within the same country were small, while larger differences were seen when comparing different European countries. Chanudet and Filella, found that in a glacial lake, more than 80% of the oxides were Fe-oxides with mean diameter of 0.29 µm, and were mostly associated with elements such as Al, Si, K, P, S, Cl or Mn [73]. In contrast, Salbu et al. studied water samples from a pit lake at a former U mine and showed that Mn and Fe were associated with the particulate fraction >0.45 µm, [74]. Skipperud et al. also studied a pit lake, a former uranium mine, for [210]Po and showed that it was mainly found in the fraction that was filtered with 0.45 µm [75]. Furthermore, Weilenmann et al. studied particle sizes in the range of 1-150 µm in two lakes and showed that the particle volume concentration distribution in surface water was centered around 7 µm and 20 µm [76].

For the sake of discussion, it can be mentioned that we performed additional samplings in 2017 when water samples were analyzed by ICP-MS before and after filtration with 0.45 µm membrane filters (unpublished data). The ratio of concentration of U in a water sample filtered with 0.45 µm to a water sample filtered with 35-40 µm was seen to be around 1 in surface water. This indicates that U was bound to particles smaller than 0.45 µm in surface water from the studied site.

## 5.2 Radiochemical procedure

All the samples presented in this work were prepared according to the procedures outlined in paper **I**, and by Pérez-Moreno et al. for [226]Ra [36]. Simultaneously, many trials were conducted on the same samples in this work in order to optimize the methods. The observations from these trials will be discussed here.

The co-precipitation with iron was a robust and reliable step and there were seldom any issues in achieving a successful precipitation. The amount of Fe added was about 10 mg per 500 g water sample. Adding twice the amount of Fe was seen to increase the yield with a couple of percent units and adding more than 40 mg of Fe caused lower yield for the same amount of reagents in the following steps. Performing the Fe co-precipitation twice, with 10 mg and then adding another 10 mg to the supernatant for the second precipitation gave even higher yields. However, this improvement in yield compared to the additional time required to perform the second precipitation may not always be feasible.

The following step required the sample to be in a nitric acid medium for the liquid-liquid extraction with tributyl phosphate (TBP). In this medium the Ra and Po among others would be in the aqueous phase and Th and U in the organic phase. Reducing the back-extraction to one time with 30 mL instead of three times with 10 mL gave similar yield. Increasing the amount of TBP from 5 mL to 10mL, reduced the possibility of Th and U being in the aqueous phase, however, more xylene was needed to dilute the organic phase in order to back-extract U and Th.

Furthermore, it was seen that one of the most time-consuming steps, changing of acid medium, could be avoided entirely. The procedure used involved drying the solution and dissolving again in the desired acid medium, which results in large volume of acid evaporations and possible losses through evaporation and adsorption to glass beaker walls.

Instead it was found to be faster to neutralize the acid with e.g. NaOH and perform a new Fe co-precipitation followed by dissolving the precipitate in the new acid medium. To reduce the amount of NaOH needed, the molarity of $HNO_3$ used for the liquid-liquid extraction of 8 M can be reduced to 4 M instead, for similar extraction strengths. Similar findings can be seen in Figure 31 in the report by James E. Grindler *"The radiochemistry of Uranium"* [77].

The Th fraction required the most amount of time as it was back-extracted from TBP with HCl and had to be in $HNO_3$ media for use with UTEVA resin. In order to reduce the time needed for the separation and purification of Th, the UTEVA resin can be omitted if preparation of the sample disc is done through micro-coprecipitation. This is because hydrogen peroxide can be added to the Th fraction prior to micro-coprecipitation with $CeF_3$ as this would not affect the IV state of Th. However, if any U would be present, it would oxidize to VI state, thus preventing a co-precipitation with $CeF_3$. It was seen that this step was sufficient enough to purify Th from U, following liquid-liquid extraction with TBP, for the studied samples in this work.

Regarding Po, the usage of Cu disc in dilute HCl was seen to be a selective method to plate Po through spontaneous deposition. Since no U, Th nor Ra would plate on Cu disc in HCl medium, the procedure of preparing $^{210}$Po could be done very rapidly. For example, following the Fe co-precipitation, the precipitate can be dissolved in dilute HCl medium with addition of ascorbic acid to complex the iron, in order to prevent it to plate on the Cu disc and worsen the resolution. The solution can then be left aside to allow the plating of Po. The yield of Po was seen to be highest for Ag discs and when plating with 80 °C for about 4 h, but yields were only slightly less with Cu discs and in room temperatures if allowed to plate for more than 4 h.

To conclude, it is important to develop and optimize radiochemical procedures and to update them when more suitable reagents and resins become available. In order to increase sample throughput and reduce costs, different combinations (synergy) of already present reagents and solvents should be studied [78]. Two references that were found useful in the study of solvents for radiochemical procedures were the reports by Moore [79] and Kumar et al. [80].

## 5.3 Water quality parameters

The measurements of pH, SC, ORP and DO in surface water could not be used to distinguish between different pit lakes (mining sites) since no parameter was unique for a certain type of mine or quarry in the present work. There was also no clear trend between any of these parameters and the activity concentration of radionuclides in surface water. Instead, the relationship with water quality parameters was found in the vertical distribution, which provided information on possible stratifications and the oxidizing or reducing conditions. The vertical distribution measurements can be valuable in determining at which depth water should be sampled, since the stratification layer position correlated with sharp gradients for some elements and all the studied radionuclides. However, the measurements of pH, SC, ORP and DO in surface water would be useful if the concentrations of various elements are already known. Then, results from such measurements can be used to monitor if major changes occur in chemical composition.

Other water quality parameters that are important for metal complexation and solubility are the dissolved organic carbon and alkalinity (carbonate concentration), respectively. Carbonate is one of the main ligands that are responsible for the solubility of U, and it would be interesting to study the correlation between the concentration of carbonates and the activity concentration of U in surface water in pit lakes.

It would also be interesting to measure pH, SC and ORP after simple tasks or operations, such as filtration of the water or adding a compound. For instance, the former could be used to assess which fraction (filtered and unfiltered) that has the highest conductivity, which could be used as an indicator of the concentration of ions. Interesting compounds to add are ligands such as ethylenediaminetetraacetic acid (EDTA) to form complex with free metals in solution. By studying the change in pH, SC and ORP before and after such operations it might be possible to gain additional insight in the chemical composition of the water.

## 5.4 Surface sediments

The surface sediments collected from the studied sites seemed to be mostly minerogenic with little organic content. Hence, good agreement between the XRF results and the type of mine were obtained, since the elements with the highest concentration in sediments reflected the composition of the ore excavated. Thus, representative rock samples from the mining site could substitute a sediment sample, since sediments from pit lakes can be more difficult to collect.

Furthermore, if samples can be measured within a day from collection and again later after the ingrowth of $^{222}$Rn, then the activity concentration of $^{214}$Pb and $^{214}$Bi from the two measurements would provide useful information on a potential disequilibrium between $^{226}$Ra and $^{222}$Rn. This procedure is usually not used for sediment samples, since the drying process usually takes several days. However, sediments could first be measured wet and later dried and weighed to obtain the mass fraction to calculate activity concentration per dry weight.

Among the surface sediments collected and measured by both alpha and gamma spectrometry, the ratio of activity concentration of $^{234}$U to $^{238}$U, taking into account the uncertainties in the activity determination, one could conclude that the two isotopes are in equilibrium. Although, the further down in the $^{238}$U decay chain, the larger is the discrepancy. The ratio of activity concentrations of $^{226}$Ra to $^{234}$Th was as low as 0.2 and as high as 2.0, and for $^{210}$Pb to $^{226}$Ra activity concentration ratios were as low 0.5 and as high as 2.7. Ratios higher than one may be due to a combination of both a loss and an increase of the activity concentration of either radionuclide. For example, a ratio higher than one between $^{226}$Ra to $^{234}$Th could be due to lower concentration of $^{234}$Th in sediments caused by a leaching of $^{238}$U. While an increase in $^{226}$Ra could be due to decay of $^{230}$Th in the surrounding or in the water, causing a supply of $^{226}$Ra that is washed down and precipitated to the sediments. Other external supplies could be from the inflow of groundwater to the pit lake. In the case for the ratio $^{210}$Pb to $^{226}$Ra, an external amount of $^{210}$Pb could originate from the decay of $^{222}$Rn in the atmosphere and in the vicinity of the pit lake. This additional Pb (and consequently Po) is what is referred to in the literature as unsupported lead [81, 82].

The two pit lakes with the largest disequilibrium in the $^{238}$U decay chain in surface sediments were the limestone quarries, one of them maintained by the municipality and advertised as a swimming resort. The larger disequilibrium at these sites could be due to the higher concentration of carbonates present (in bedrock and quarry) which efficiently solubilize $^{234}$U that has become exposed to the water, and also through cation exchange by the abundant Ca at these sites. The latter has been seen to increase the solubility of U by displacing it from soil, forcing it into solution [15, 50].

For the $^{232}$Th decay series, the disequilibrium seen in the chain was less pronounced and practically all radionuclides were in equilibrium when measuring the sediments approximately two months after sampling. This is mainly due to relatively shorter half-lives among the progeny, e.g. $^{220}$Rn has a half-life of 56 s, which hinders any long-distance transport.

It is also important to consider the size of the collected sediment particles when studying the equilibrium in the decay chains. Assuming that the outer surface layer of sediment particles are weathered and some radionuclides are leached out, the surface layer (and content) can be too small for potential disequilibria to be detected, when including the overall content of the sediment particle. This issue is even more important to consider when using gamma spectrometry, since the uncertainties can be up to 20 % or higher for a coverage factor of 2 ($\approx$95 % confidence). For example, assuming that only 50 µm of the outer layer of a 1 mm spherical particle is weathered with a disequilibrium such that $^{234}$U to $^{238}$U ratio is 0.5, then the volume of this layer is only about 14 % compared with that of the whole particle. If the ratio of $^{234}$U to $^{238}$U is 1 in the remaining part of the particle, then the sum $(0.5 \cdot 14\% + 1 \cdot 86\%)$ would be 0.93, which is well within the uncertainty of gamma spectrometry results.

## 5.5 HCA and PCA

In the present work, HCA and PCA were used to find similarities among measured parameters and studied sites (pit lakes) by identifying clusters, high loading values and groups in score plots. However, PCA can also be used for other purposes, such as tracing the source (input) of contaminants in sediments by spatial sampling [83, 84], and as a risk model [85]. The latter was achieved by calculating a PCA score for a sample and comparing the score with a reference score that reflects an uncontaminated site.

In the reviewed publications where PCA was applied on water and sediment samples, Zn was included in most of the studies, and the following elements were found in the same component as Zn: Pb [83, 86-89], Fe [84, 85, 89, 90], Cd [83, 86, 88], Cu [84, 86, 87], Cr [85, 86], Ni [83, 86], and U [86, 88]. It is worth to mention that among these publications only two included U and demonstrated Zn in the same component as U. Although U and Zn were not seen in the same component in paper **IV**, it was observed that Pb and Cu were in the same component as Zn (Table 3 in paper **IV**). This relation could also be seen in HCA where a cluster was found between Zn, Pb and Cu (Figure 1a, paper **IV**).

From the PCA and HCA results in paper **IV** and also in Figure 6, the majority of pit lakes were grouped around the origin or clustered together. For a pit lake to be positioned around the origin means that the product sum of loadings and the standardized concentrations or values are low (close to 0). As the standardized concentrations and values depend on the pit lakes included (standardization uses the mean and standard deviation), then PCA score plots can differ depending on which pit lakes are included in the analysis.

Similarly, the loadings in each component depend on the parameters included. For example, as the concentration of Ca and specific conductance was seen to be highly correlated, then these would together receive a high loading value for a particular component (they are important in explaining the variance). However, if one of them was removed then the other parameter would not by itself explain the variance and would receive a lower loading value. Furthermore, as the sum of products is calculated, it is also possible that some products are negative and some are positive, resulting in a sum close to zero.

One possibility that were not tested due to the small number of analyzed sediment samples is to use ratios between the concentration of an element in surface water and in sediment as input parameters in PCA and HCA. As seen in Figure 5, the concentration of Ca in surface water might not be the optimal parameter to characterize different pit lakes (mining sites). However, the concentration of Ca in sediments were higher in limestone quarries than in some of the limed lakes, and thus such a ratio would differentiate the pit lakes better. Finding a ratio or a mathematical expression that identifies certain types of pit lakes can be valuable in modeling purposes, with better characterization of the lakes.

## 5.6 Vertical distribution

The vertical distribution measurements at the studied site provided insight on the magnitude of variation and the relation between water quality parameters and the concentration of elements and radionuclides. The change in ORP and DO from oxidizing to less oxidizing and anaerobic conditions, coincided with concentration of Fe and Mn, possibly due to a reduction in oxidation state from III to II causing a redissolution of Fe and Mn precipitates (also release of adsorbed elements). The increase in Fe concentration near the bottom of the lake compared with that at the surface was a factor of 120. A more dramatic increase was seen by Green et al. in a study of a 75 m deep lake were the Fe increased by a factor of 1075 at 68 m depth [91]. They also observed a similar vertical distribution for Mn and Zn with an increase towards the bottom where the concentration of Zn had a slightly broader peak than Fe and Mn. A broader peak of Zn was also seen in the present work, but around half the depth of the lake (30 m)

To answer the question on how well a surface water sample represents the distribution of stable elements and radionuclides within the entire pit lake, the answer is that a surface water sample is not representative for lakes not well mixed. Among the mining sites included in this work, only one site had a visible sign indicating that the pit lake (limestone quarry) is used as a water reservoir. However, most mining sites studied were located in the countryside where local habitants receive their water from private wells, which in some cases are only tens of meters away from the pit lake. The pit lake used as a water reservoir had the water pump located at about 10 m depth where the water was filtered through a mesh filter and exposed to UV light (to kill bacteria), supplying approximately 100 habitants with drinking water. As was seen in the vertical distribution of the radionuclides, the depth of the water pump can be important in stratified lakes in order to reduce ingested radionuclides. Figure 4 in paper **V** shows that the activity concentration in surface water can underestimate the activity concentration in the lake body as much as a factor of five for $^{226}$Ra and a factor of six for $^{210}$Pb and $^{210}$Po. For (pit) lakes that are used as a drinking water reservoir, similar studies should be conducted to investigate a suitable depth of the water pump in order to reduce ingestion of naturally occurring radionuclides.

## 5.7 Dose assessment

For the purpose of estimating radiation dose from drinking water supplied from pit lakes, one could ask if there is one radionuclide that could be measured in order to ensure that the recommended dose from drinking water in Sweden, 0.1 mSv/y [59], is not exceeded. From the data included in this work, such an assumption is not supported; rather it is implied that to get an accurate estimate of radiation dose you need to measure the different radionuclides. However, the pit lake with the highest measured activity concentration of $^{238}$U also had the highest measured activity concentration of all the other studied radionuclides. Thus, for sufficiently high activity concentrations, in this example 1200 mBq/kg of $^{238}$U, one could expect to find high activity concentrations of other radionuclides also. This was, however, not seen in the pit lake with the second highest activity concentration of 740 mBq/kg of $^{238}$U, and at one site where the activity concentration of $^{238}$U was below 1 mBq/kg, the ratio of the activity concentration of $^{210}$Po to that of $^{238}$U in surface water was 16.

For the pit lakes where $^{226}$Ra and $^{210}$Pb were measured, the ratios of the activity concentration of $^{226}$Ra to $^{238}$U varied from 0.02 to 8.1, and from 0.008 to 8.0 for $^{210}$Pb to $^{238}$U. The highest ratio of 8 for both $^{226}$Ra and $^{210}$Pb was found in the same pit lake, a former silver mine with high concentration of Pb in surface water and a pH of 4.9. As a comparison, the ratios of the dose coefficients Sv/Bq (ingestion) to $^{238}$U is 1.1 ($^{234}$U) : 4.7 ($^{230}$Th) : 6.2 ($^{226}$Ra) : 26.7 ($^{210}$Po) : 5.1 ($^{232}$Th) [92]. For the pit lake with highest $^{238}$U activity concentration mentioned above (1200 mBq/kg), the annual effective dose contribution using coefficients from ICRP publication 119 (Table F.1, Adult), assuming an annual ingestion of 730 L per year [59], are $^{238}$U: 39 nSv, $^{234}$U: 61 nSv, $^{230}$Th: 4.0 nSv, $^{210}$Po: 83 nSv and from $^{232}$Th 1.5 nSv. It should be mentioned that $^{226}$Ra was not analyzed in this pit lake, but in the nine pit lakes where $^{226}$Ra was measured the activity concentration was on average 5 times higher than for $^{210}$Po; using this value the dose contribution from $^{226}$Ra would be 97 nSv (highest contribution). Adding the above dose contributions would give about 0.3 mSv per year, and comparing with the average annual dose received by the general public from natural sources of 2.4 mSv [93], this is 12%. However, if this water is also used for irrigation of local crops, water for livestock and habitat for fish, the bioaccumulation of radionuclides in the food chain would likely give a higher end contribution.

# 6 Conclusion

This thesis summarizes the main findings from the overall aim of this work which was to increase the knowledge on the activity concentration of naturally occurring radionuclides that can be found in Swedish pit lakes, originating from non-uranium mines. The conclusions related to the specific aims are summarized as follows:

Since the set-up of the radiochemistry laboratory, participation in international exercises have continued with satisfactory results. Apart from U, Th and Po isotopes, Ra isotopes are nowadays also being routinely measured. Continued and successful work has been achieved in increasing the yield of radiochemical procedures, especially for Th isotopes through microprecipitation (**paper I**).

Pit lakes in Sweden originating from non-uranium mines had activity concentrations of naturally occurring radionuclides well below the recommendations for drinking water. The activity concentration in surface water from the studied sites showed that the pit lakes in Southern Sweden had on average a factor of ten higher activity concentration of U isotopes and three times higher for $^{210}$Po and Th isotopes than the pit lakes in Northern Sweden. For surface sediments, the activity concentrations in Southern Sweden compared to Northern Sweden were a factor ten for $^{238}$U, factor two for $^{232}$Th and a factor one for $^{40}$K (**papers II, III**).

Despite the different types of mines included in this work, the concentration of the most common elements found in Earth's crust varied relatively little among the pit lakes, even less so in surface water. It was instead the trace elements that seemed to distinguish the different pit lakes from each other. The findings from the statistical analysis suggest that the ambient dose equivalent rate can be used to locate sites with higher activity concentration of radionuclides in sediments and in surface water (**paper IV**).

Furthermore, the activity concentration of radionuclides in surface water may not be representative of the lake as a whole. In a stratified lake included in this work, the activity concentration near the bottom of the lake was up to a factor of six higher compared with the activity concentration in surface water. If sampling is limited to one water sample and it is possible to access the deepest part of the pit lake, then the water sampling depth should coincide with the depth at which the specific conductance reading is the highest. This could in the best case ensure that the water sampled contain the highest concentration of elements and radionuclides that can be found in that pit lake (**paper V**).

# 7 Future perspectives

For future studies of pit lakes, it is recommended that one or two elements from each chemical group, alkali and alkaline earth metals, and transitional and post-transition metals, should be included apart from the elements and radionuclides of interest. Alkalinity and total dissolved carbon should also be measured in order to study their relation to the concentration of naturally occurring radionuclides.

It is also advised that sediment or rocks, and water samples should be collected from each studied site, in order to calculate ratios for concentration of elements and radionuclides from the two types of samples. These ratios should then be compared and preferably used in PCA to explore similarities and dissimilarities, in order to further explore how the different sites can be characterized.

To further increase the knowledge on the vertical distribution of elements and radionuclides in stratified pit lakes, it would be interesting to study the relative change of specific conductance and redox potential and compare with the relative change in concentration of elements and radionuclides. If the findings lead to consistent trends seen among many different pit lakes, then a relation among the parameters can be developed for an assessment of the vertical distribution of radionuclides, following in-situ measurements of specific conductance and redox potentials.

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**II**

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**IV**