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# **MOBILIZATION OF NATURAL URANIUM SERIES RADIONUCLIDES AT THREE MINING SITES IN FINLAND**

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ACADEMIC DISSERTATION

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*In loving memory of my father*

*'My father gave me the greatest gift anyone could  
give another person, he believed in me.'*

Jim Valvano



## ABSTRACT

Northern Fennoscandia has experienced an unparalleled mineral exploration boom since around 2005. At the same time, there has been increasing awareness of the potential environmental impact of non-nuclear industries that extract and/or process ores containing naturally occurring radionuclides. Industrial activities may result in significant environmental problems if the waste generated during ore processing is not adequately managed. In 2010, a new project was launched with an objective to study the mobility of uranium series radionuclides from diverse mill tailings in a northern boreal environment in Finland. Three sites were investigated: the Talvivaara Ni-Cu-Zn-Co mine in central Finland, a former phosphate mine at Sokli, Finnish Lapland, and a former pilot-scale uranium mine at Paukkajanvaara, eastern Finland.

The mobility of radionuclides from the mill tailings at Sokli was examined in order to assess the potential environmental impact of past and future mining activities. Mineralogical studies did not indicate that uranium or thorium have been mobilized from altered pyrochlore-group minerals in the Sokli ore or tailings. In the tailings pond, no clear trends were observed in the activity concentrations of uranium, radium or thorium isotopes in the surface layers of the mill tailings. In subsurface samples, an increase in the concentration of these isotopes can be seen when approaching the pond at the distal end of the sludge field. However, this increase is most likely to a consequence of compositional changes in material discharges. The results of the sequential extraction tests suggested that neither uranium nor thorium is in an exchangeable form and could potentially be released to the environment. Uranium (4% of the total concentration) was partly soluble under weakly acidic conditions, whereas thorium was tightly bound in mineral phases.

At the former Paukkajanvaara uranium mine in Eno, the aim of the study was to examine the potential for further mobilization of radionuclides after remediation of the site in early 1990s. There are two primary sources of contamination at the site, the waste rock pile and the tailings. The results indicate that  $^{226}\text{Ra}$  has been leached from the waste rock pile and accumulated in surrounding soil. In run-off sediment samples collected from a dry stream bed near the waste rock pile, the activity concentrations of  $^{226}\text{Ra}$  and  $^{238}\text{U}$  are higher than in soil samples. From the tailings, radionuclides can leach directly to the lake and to another small stream, which flows to the east of the waste rock pile. The results from the soil samples collected between the tailings area and the stream indicate leaching of  $^{238}\text{U}$  and  $^{226}\text{Ra}$  with the surface flow. Sediment samples collected from the bottom of the lake display pronounced uranium series disequilibrium with fractionation of  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  relative to the parent  $^{238}\text{U}$ . The results therefore indicate that leaching

and accumulation of at least  $^{226}\text{Ra}$  from the waste rock pile and possibly tailings is still ongoing.

At Talvivaara, the aim of the study was to generate new data leading to a better understanding of the fate of radiotoxic uranium daughter nuclides, primarily  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ , in the mining process. In heap leaching, uranium is dissolved from uraninite to the pregnant leach solution. Uranium is probably transported as uranyl ions and uranyl sulfate complexes in the acid pregnant leach solution (PLS), and finally ends up in precipitates of the gypsum pond tailings via iron removal and final neutralization processes during the removal of residual metals. In terms of radiation safety, the  $^{238}\text{U}$  activity concentration in the gypsum pond is partly above the exemption value (1000 Bq/kg) for natural radionuclides of the  $^{238}\text{U}$  series. Radium and thorium mostly stay in the heaps during heap leaching. In addition,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  stay mainly in the heaps but slight mobilization of these nuclides was indicated. Secondary sulfate minerals, such as gypsum and jarosite, are precipitated from the sulfate-rich and acid PLS at Talvivaara. These minerals can incorporate radium in their crystal lattices, limiting  $^{226}\text{Ra}$  mobility. Therefore, it can be assumed that most of radium and possibly part of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  are co-precipitated with poorly soluble sulfates in the Talvivaara heaps.

## ACKNOWLEDGEMENTS

“It is not the mountain we conquer, but ourselves.” — Edmund Hillary

Pursuing a Ph.D project is just like climbing a high peak, step by step, accompanied with tiredness, hardships, frustration, joy, encouragement and trust, and with so many people’s kind help. When I found myself at the top, I realised that it was actually team work that got me there. Undertaking this PhD has been a truly life-changing experience for me and it would not have been achievable without the support and guidance that I received from many people.

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## LIST OF ORIGINAL PUBLICATIONS

Paper I: Tuovinen, H., Pohjolainen, E., Read, D., Solatie, D. and Lehto, J. 2015. A comparison of analytical methods for determining uranium and thorium in ores and mill tailings. *Journal of Geochemical Exploration*, 148, 174-180.

Paper II: Tuovinen, H., Vesterbacka, D., Lempinen, J., Pohjolainen, E., Read, D., Solatie, D. and Lehto, J. 2015. Radionuclide and heavy metal redistribution at the former pilot-scale apatite plant in Sokli, northern Finland. *Boreal Environment Research*, 20, 350-362.

Paper III: Tuovinen, H., Pohjolainen, E., Vesterbacka, D., Kaksonen, K., Virkanen, J., Solatie, D., Lehto, J. and Read, D. Release of radionuclides from waste rock and tailings at a former pilot uranium mine in eastern Finland. *Submitted*.

Paper IV: Tuovinen, H., Pohjolainen, E., Lempinen, J., Vesterbacka, D., Read, D., Solatie, D. and Lehto, J. 2016. Behaviour of radionuclides during microbially-induced mining of nickel at Talvivaara, eastern Finland. *Journal of Environmental Radioactivity*. 151, 105-113

The author planned and executed the majority of the experimental work for all publications. Mineral characterizations in publications I, II and III were done by coauthors at the Geological Survey of Finland. Some of the gamma and alpha measurements in publications I-IV were performed by coauthors at the Finnish Radiation and Nuclear Safety Authority (STUK) or at the University of Helsinki. All manuscripts were written by the author.

## ABBREVIATIONS

AMD	acid mine drainage
EPMA	electron probe micro-analysis
ICP-MS	inductively coupled plasma mass spectrometry
NORM	naturally occurring radioactive material
PLS	pregnant leach solution
UMT	uranium mill tailings
XRD	X-ray diffraction
XRF	X-ray fluorescence

# 1 INTRODUCTION

## 1.1 NATURAL RADIONUCLIDES IN MINING INDUSTRY

Considerable concerns surround the potential introduction of Naturally Occurring Radioactive Material (NORM) into the environment as a result of mining activities (Bhattacharyya 1998). Each uranium-bearing ore body has the potential to produce NORM wastes with different concentrations of uranium, thorium and their daughter nuclides, depending not only on the extraction procedures, but also on the initial concentrations and chemical forms of the naturally occurring radionuclides in the mineral matrices (Paschoa 1998). Natural radionuclides, especially those generated from the uranium-thorium decay series, may leach from rock waste or tailings with time and contaminate local water and soil resources and pollute drinking water (Darko et al. 2009). Other potential exposure pathways include dust dispersion and bioaccumulation through the food chain.

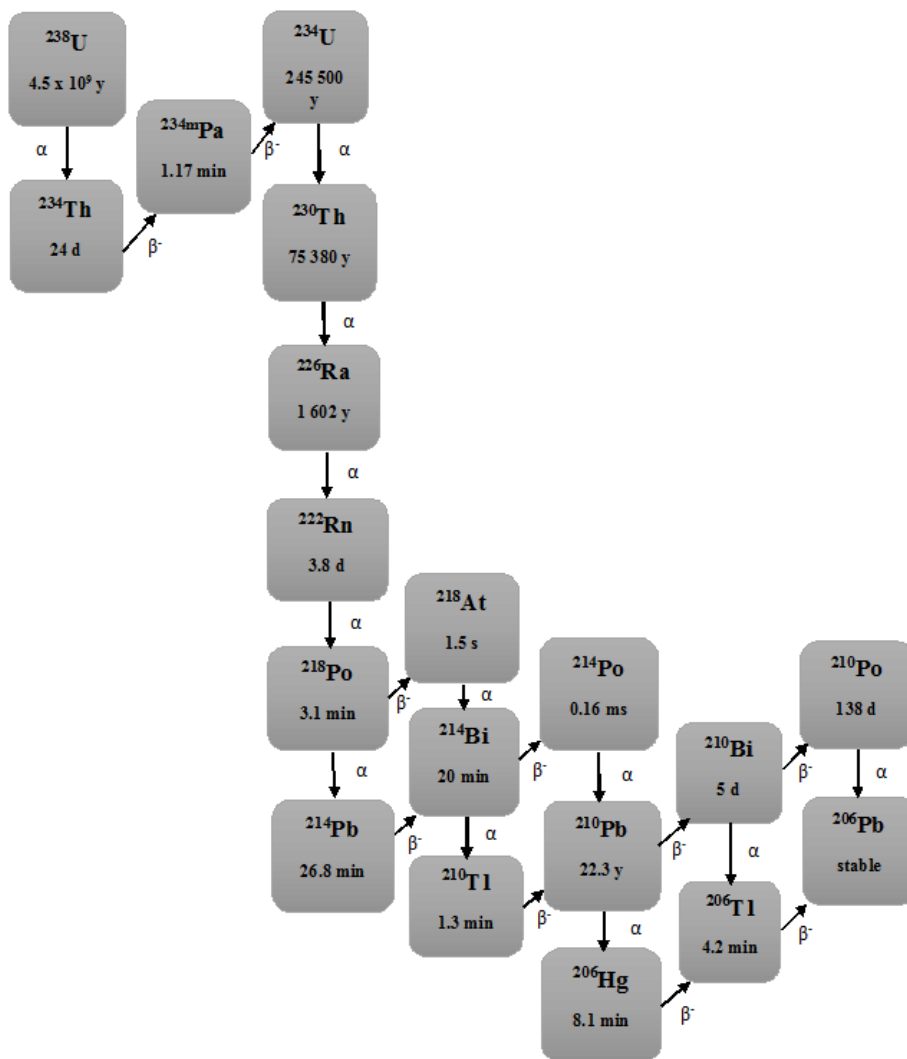
Over time, uranium mill tailings undergo chemical reactions in a tailings repository, and their mineralogy and pore water composition may change. Any dissolved radionuclides, metals, and metalloids may thereby persist in solution, precipitate or co-precipitate by interacting with other components in tailings, such as sulfates or metal hydroxides, or be adsorbed by tailings solids (Benes et al. 1984, Landa 1991, Landa 1999, Landa and Grey 1995). Processes acting to keep contaminants dissolved in tailings solutions include sulfide oxidation and acid mine drainage (AMD) development, leaching by residual process chemical, bacterial action, and reductive dissolution of Fe and Mn oxyhydroxides (Landa et al. 1991, Lottermoser 2003). The behavior and fate of radionuclides needs to be understood in order to select appropriate rehabilitation techniques. In contrast, measurements and analyses performed well after rehabilitation of a tailings repository allow the determination of active processes and critical evaluation of the applied rehabilitation technique. Studies of tailings impoundment in which the predictions made during mine closure are compared with actual post-rehabilitation data are rare (Lottermoser and Ashley 2005).

The primary aim of this study was to examine the mobilization of uranium and its radiotoxic daughter nuclides from diverse mill tailings in order to assess the potential environmental impact of past and future mining activities. The results will play an important role in estimating radiation doses to the local population. Three diverse mining sites were chosen to this study: a former pilot-scale apatite

plant at Sokli, northern Finland, a former uranium mine in Eno, eastern Finland, and the Talvivaara nickel mine in Sotkamo, eastern Finland.

## 1.2 URANIUM DECAY SERIES

Uranium occurs in the Earth's crust at a mean concentration of about 3 ppm, though it tends to be higher in granitic terrains. Uranium exists in the bedrock as a wide range of mineral phases, the most important of which being uraninite  $\text{UO}_2$ , in which uranium is present in its lower valence state of IV, and pitchblende, in which uranium has a net valence state between IV and VI. In addition, there are a wide range of secondary phases, principally silicates and phosphates, in which the valence state of uranium is VI. Uranium has three isotopes in nature,  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$ , of which the last one is responsible for 99.3% of the total mass.  $^{235}\text{U}$  and  $^{238}\text{U}$  along with the thorium isotope  $^{232}\text{Th}$  are the parent nuclides of the natural decay series, leading to the stable lead isotopes  $^{207}\text{Pb}$ ,  $^{206}\text{Pb}$  and  $^{208}\text{Pb}$ , respectively. Figure 1 presents the decay chain of  $^{238}\text{U}$ . Among the progeny of  $^{238}\text{U}$  ( $t_{1/2} = 4.5 \times 10^9$  y), there are several important radionuclides with respect to the radiation doses affecting humans.  $^{222}\text{Rn}$ , an inert noble gas, is the most important of them, constituting more than half of the average radiation doses to the Finnish population (STUK). Radon occurs in a gaseous form and therefore diffuses into the atmosphere, from which its daughters ( $^{210}\text{Pb}$ ,  $^{210}\text{Po}$ , and short-lived lead, polonium and bismuth isotopes) deposit on the earth's surface, attached to aerosol particles. Of the other radionuclides,  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$ ,  $^{210}\text{Po}$ , and  $^{238}\text{U}$  are responsible for a large fraction of the doses to humans. The first three of these are regarded as the most radiotoxic radionuclides when ingested or inhaled. This study focuses on  $^{238}\text{U}$  and its three radiotoxic daughter nuclides mentioned above.



**Figure 1.** Natural  $^{238}\text{U}$  decay chain

$^{226}\text{Ra}$ , which has a half-life of 1602 years, always exists in uranium ores (Bhattacharyya 1998).  $^{226}\text{Ra}$  is formed by the alpha decay of  $^{230}\text{Th}$  and further decays by alpha decay to  $^{222}\text{Rn}$  (Fig. 1). Radium always appears in oxidation state of +II, and its compounds are relatively soluble.  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  are late members in the uranium decay series, with  $^{210}\text{Po}$  being the granddaughter of  $^{210}\text{Pb}$  (Fig. 1). Although  $^{210}\text{Po}$  is the longest-lived isotope of polonium in nature, its half-life is only 138 days. The half-life of  $^{210}\text{Pb}$  is considerably longer (22.3 y); they are in equilibrium in most cases in the geosphere. Even though the half-life is so short,  $^{210}\text{Po}$  is always present in the environment because it is maintained by its parent nuclide  $^{210}\text{Pb}$ , which decays by beta emission through  $^{210}\text{Bi}$  to  $^{210}\text{Po}$ . Polonium forms compounds in the oxidation states of -II, +II, and +IV. The most common oxidations state is +IV, in which

form Po is only sparingly soluble in natural waters, at their typical pH of about 5-9, tending to become attached to particulate matter. Under reducing conditions, polonium can also occur in the oxidation state of +II. The most common oxidation state of lead is +II. Under extremely oxidizing conditions, the oxidation state of +IV is also possible. Most lead compounds are sparingly soluble, in particular lead sulfide (PbS) and lead sulfate (Lehto and Hou 2011).

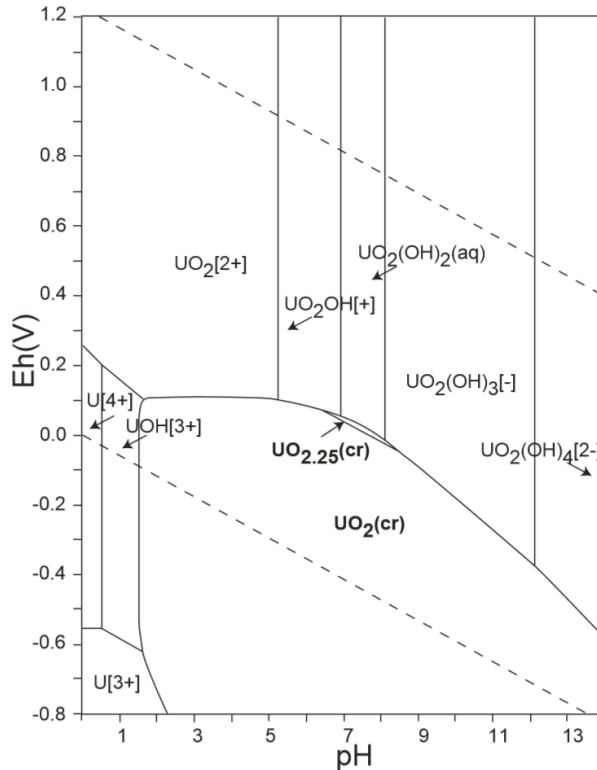
### 1.3 MOBILIZATION OF RADIONUCLIDES FROM TAILINGS

The mobility of radionuclides is of prime importance in risk assessment. It is well known that uranium occurs in varying concentrations in the ores and tailings and in more than one physicochemical form, ranging from loosely held physically adsorbed ions to tightly fixed components in crystal lattices. Depending on the transport history of uranium, its daughters may be present in various amounts (Bhattacharyya 1998). In particular, tailings solutions resulting from acid leaching tend to contain high concentrations of soluble and dissolved radionuclides, metals and sulfate, unless the tailings material is neutralized prior to discharge to the tailings storage facility. In such acid-leached tailings, the mobilization of radionuclides from tailings solids into tailings solutions may occur after tailings deposition, even long after rehabilitation of the tailings repository has been completed (Bhattacharyya 1998).

As stated previously in section 1.2, the most common uranium oxide is  $\text{UO}_2$ , in which uranium is chemically immobile in the +IV oxidation state. It is very stable over a wide pH range under reducing conditions, but as the conditions become more oxidizing, uranous species are oxidized to uranyl species  $\text{UO}_2^{2+}$  (Langmuir 1978), in which uranium is in its chemically mobile +VI state (Fig. 2). The mobility of uranium is enhanced by orders of magnitude when it is oxidized to its hexavalent state. Additionally, uranyl complexes in the range of natural conditions are more stable than uranous complexes (Langmuir 1978). The solubility of uranium also depends on the mineralogical occurrence of uranium. When uranium is held in minerals like uraninite ( $\text{UO}_2$ ) or calcite ( $\text{CaCO}_3$ ), it may leach from the solid phase in suitable circumstances. In acidic water (pH <6), uranium forms complexes, especially with sulfate, phosphate, and fluoride ions, but in neutral and alkaline solutions, uranium occurs practically solely as carbonate complexes (Lehto and Hou 2011). The presence of uranium as anionic carbonate complexes makes uranium very soluble and mobile in groundwater. In surface water, hydrolysis competes with carbonate complexation to some extent. When the acid concentration decreases below 0.5 M, tetravalent uranium starts to hydrolyze and at pH above 4, the prevailing species is the neutral soluble species  $\text{U}(\text{OH})_4(\text{aq})$ . Hexavalent uranium also hydrolyzes, but not as strongly as tetravalent uranium. At pH of 5-6, the prevailing species is  $(\text{UO}_2)_3\text{O}(\text{OH})^{3+}$ . The importance of organic substances in complexing with uranium



is also known. Generally, organic substances play an important role in uranium adsorption under acidic conditions (Crancon and Lee 2003, Silva and Nitsche 1995). However, even in these circumstances, at pH of >6.5 carbonate complexes are the predominant species.



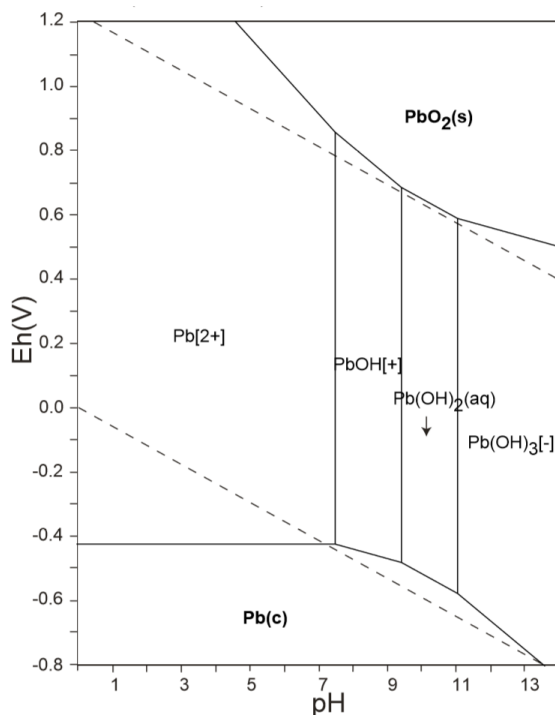
**Figure 2.** Eh - pH diagram of uranium in  $10^{-10}$  M solution (Atlas of Eh-pH diagrams, Geological Survey of Japan Open File Report No. 419, 2005).

Radium is soluble and mobile under acid conditions but high sulfate concentrations in acid solutions limit the solubility of Ra (Lottermoser 2007). As an alkaline earth metal, radium replaces other metals of the same group (Ba, Sr, Ca), especially barium. At the rock-water interface, the energy of recoil received by radium atoms during alpha decay may help release the radium into the water phase (Vesterbacka 2005). However, once in the water phase as a divalent positive ion, it is not totally soluble, but adsorbs on rock surfaces through ion exchange or precipitation. In low saline waters, radium occurs as uncomplexed  $Ra^{2+}$  cations (Vesterbacka 2005). Weak complexes with chloride, sulfate and carbonate anions are possible in saline waters, but in low saline water, these have no effect on the transport of radium. The colloidal transport of radium has been less studied, but analogously with barium,

it can be assumed that colloid formation could also act as a transport mechanism for radium (IAEA 1990).

The only  $^{210}\text{Pb}$  compounds that dissolve in water are the acetate, nitrate, chlorate, and perchlorate. Sparingly soluble  $^{210}\text{PbSO}_4$  can be dissolved in excess acetate or hydroxide. In groundwater, Pb is found in an inorganic form, complexed with organic matter and adsorbed onto particles (Vesterbacka 2005). In acid groundwater, at a pH of less than 6, Pb exists as an ionic form (Fig. 3). Hydrolysis products begin to form only at pH of 6 (Ulrich and Degueldre 1993). These hydrolysis products easily form compounds and therefore Pb is often bound in inorganic and organic colloids (Lehto et al. 1999, Lieser and Ament 1993a, Lieser and Ament 1993b, Vaaramaa et al. 2003).

Polonium occurs as the  $\text{Po}^{4+}$  ion in acidic solutions and forms complexes with acid anions. At pH values above 2.5, polonium begins to form colloids. In weakly acidic and neutral groundwater, polonium occurs as  $\text{PoO}(\text{OH})^+$ ,  $\text{PoO}(\text{OH})_2$  and  $\text{PoO}_2$  and at pH of 7, sparingly soluble  $\text{Po}(\text{OH})_4$ . At higher pH, polonium appears as negative colloidal hydrolysis products until pH of 12, when it dissolves as the polonate  $\text{PoO}_3^{2-}$  ion. The predominant oxidation state of Po is +IV, and thus Po is sparingly soluble to natural waters at pH of 5-9. However, under highly reducing conditions, it can appear in the oxidation state of +II (Lehto and Hou 2011).



**Figure 3.** Eh - pH diagram of lead (Atlas of Eh-pH diagrams, Geological Survey of Japan Open File Report No. 419, 2005).

After mobilization from their original source, radionuclides may persist in the solution or be reprecipitated by various mechanisms, such as sorption, co-precipitation, ion substitution, and redox transformation. The formation of secondary minerals can lead to a substantial natural accumulation of radionuclides in local epigenetic zones, called geochemical barriers, where conditions are distinctly changed. Manganese and iron oxides formed by a variety of mechanisms are important scavengers of contaminants (Landa 1982, Jones et al. 2006). Jarosite, a secondary sulphate, can also be an important host for environmental contaminants and has been shown to concentrate  $^{226}\text{Ra}$  and lead (Kaiman 1978, Landa 2004). Gypsum is major host of radium in fresh, acid-leach/lime-neutralized uranium mill tailings (UMT). For aged tailings, the predominant  $^{226}\text{Ra}$  hosts are iron-oxyhydroxides along with barium and lead sulfates (Somot et al. 1997, Somot et al. 2000, Somot et al. 2002).  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  can also coprecipitate with sulfates, whereas co-precipitation with  $\text{CaCO}_3$  is minimal (IAEA 1990). Under changing redox conditions, radionuclide accumulations can be remobilized by chemical or microbiological mechanisms (Ivarson et al. 1976, Jones et al. 2006)

## 1.4 RESEARCH PROBLEM AND OBJECTIVE

Based on earlier studies both in Finland and in other countries, it is expected that several key radionuclides present at the study sites have the potential to be mobilized and transported in local water systems, if the wastes are not adequately managed. Uranium is expected to be the most soluble via formation of soluble sulfate complexes in the acidic waste environment and hydroxyl-carbonate complexes species as the pH rises. Radium, polonium and lead are also expected to be leached from the ore minerals and partly co-precipitated as sulfates.

In this study, answers to the following questions are looked for:

- 1) Which mineral phases control radionuclide distributions in the ores and mill tailings?
- 2) What is the isotopic fractionation of natural U series nuclides caused by mineral processing?
- 3) Which factors affect the leaching of radionuclides from the ores and mill tailings?
- 4) What is the aqueous speciation of radionuclides in contact with the mill tailings?

## 2 STUDY SITES

Three mine sites were chosen to this study: the Talvivaara nickel mine, a former pilot-scale apatite mine at Sokli and a former uranium mine at Paukkajanvaara (Fig. 4). The sites were chosen based on the diversity in ore characteristics, mining process, and history of the mine site, excluding the Talvivaara mine, which is still in operation.

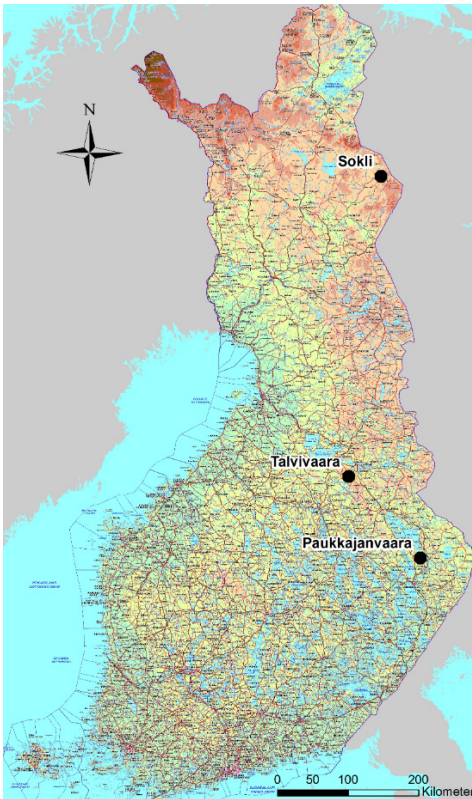


Figure 4. Site locations

### 2.1 SOKLI

Sokli is located in the north-eastern part of the municipality of Savukoski ( $67^{\circ}48'N$  and  $29^{\circ}18'E$ , 220 m above sea level) close to the headwaters of the Nuorttijoki River and within the catchment of its tributary Soklioja. The Nuorttijoki River flows to a lake, Nuorttijärvi, in Russia. Sokli is located 100 km from the centre of Savukoski and the border of Russia is 12 km to the east. The Sokli carbonatite complex is the westernmost deposit of the Devonian (ca. 365 Ma) Kola Alkaline Rock Province (O'Brien and Hyvönen 2015). Similar deposits in Russia include Kovdor, Afrikanda and Lovozero (Fig. 5).



**Figure 5.** Principal deposits of the Kola Alkaline Province.

The Sokli carbonatite was discovered in 1967 and at the end of the 1970s, pilot-scale mining and mineral processing took place at the site. The latter did not include chemical treatment of the apatite ore; processing was limited to removal of gangue minerals by physical methods. The mill tailings were deposited adjacent to the concentrating facility. The deposit is presently being developed for beneficiation of the regolithic phosphate ore which overlies the magmatic carbonatite. In addition to the phosphorus ore, the carbonatite massif contains other commodities, such as niobium, iron,

and vermiculite. The mineral deposits have a high concentration of both uranium and thorium in the middle of the massif (O'Brien and Hyvönen 2015).

## 2.2 PAUKKAJANVAARA

Paukkajanvaara is located in eastern Finland, 50 km from Joensuu (Fig. 6) (N 6981372 E 653304, ETRS-TM35FIN). The region belongs to the southern boreal vegetation zone. The Paukkajanvaara uranium mineralization occurs at the contact of Paleoproterozoic sandstones and mafic dikes, with uraninite and uranophane being the main uranium minerals (Pirainen 1968). Mining operations were started at Paukkajanvaara in 1959. The mine was basically a test site for assessing the feasibility of larger-scale uranium mining. The ore was milled and enriched at the mining site. Mining proved to be uneconomic, and the operations ceased in 1961 after producing 30 t of uranium from 40,000 t of ore grading 0.14 wt% U (Pohjolainen 2015). In the late 1970's, the entrance of the mining shaft was covered with a concrete slab and the rest of the area including tailings, waste-water ponds etc., were abandoned. They were left untouched for nearly 30 years until the Finnish Radiation and Nuclear Safety Authority (STUK) initiated a review. Their results indicated that radiation levels at the site had been increased by 0.5  $\mu$ S/h as a direct result of the mining operations. Rehabilitation commenced in 1992 and was complete by 1994. The mine shaft and pit were demolished and the entire

area, including tailings, was first covered with 30 centimeters of clay, on top of which 1.2 meters of till was placed. The small ponds and stream sediments were not removed. A final inspection of the area was carried out in August 1994 and the area was released without restrictions for outdoor use.



**Figure 6.** Location of the historic pilot-scale uranium mine at Paukkajanvaara, eastern Finland.

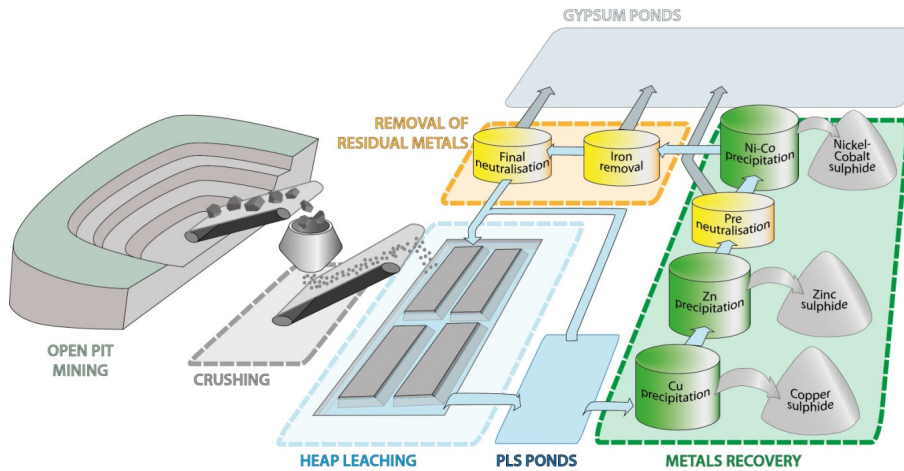
## 2.3 TALVIVAARA

The Talvivaara open pit mine is located in Sotkamo, eastern Finland (63° 58' 30" N, 28° 0' 30" E, WGS84). The mine area is approximately 60 km<sup>2</sup>. The landscape in the area is typical for Kainuu, containing alternating swamps, ponds, lakes, and forests (Pöyry Finland Oy 2013). The mine area is situated at the watershed of Vuoksi and Oulujoki Rivers and the waters from the mine end up in both water systems. The drainage system near Talvivaara consists mainly of

small lakes and streams. pH and buffering capacity are low. In some places in the water systems, the metal concentration is naturally high (Parviainen et al. 2014).

The Talvivaara mine is associated with a Paleoproterozoic black schist-hosted Ni-Cu-Zn-Co deposit (Kontinen and Hanski 2015). It has been in operation since 2008. The company uses the bioheap leaching technique to extract metals (Ni, Zn, Cu, Co) from low-grade black schist, which also contains uranium with an average concentration of 17 ppm (Kontinen and Hanski 2015). The production process at Talvivaara includes open-pit mining, crushing, heap leaching, metals recovery and removal of non-valuable residual metals (Fig. 7). The leaching solution is collected at the bottom of the heaps and either re-circulated through the heap or fed to the metal recovery unit. After two years of primary leaching, the ore is unloaded and re-stacked for secondary leaching to recover metals from poorly leached material. The secondary leaching heap will also be the final disposal site for leached ore. In metals recovery, copper, zinc, nickel and cobalt are precipitated from the pregnant leach solution and filtered to produce saleable metal products (Pitkäjärvi 2009). After the valuable metals are recovered, the solution is further purified from residual metals and returned to irrigate the heaps. During the two-stage removal of non-valuable

residual metals, the residual solution is neutralized and the remaining metals are removed from it. The slurry is thickened and the thickener underflow is directed to the gypsum ponds (Talvivaaran Kaivososakeyhtiö Oyj 2012, Lapin vesitutkimus Oy 2012). In 2010, Talvivaara announced its plans to recover uranium as a by-product, resulting from the fact that uranium mostly dissolves in the pregnant leach solution (PLS) during heap leaching. Currently, dissolved uranium mostly ends up in the gypsum pond tailings and partly in the Ni-Co sulfide concentrate product (OECD 2014).



**Figure 7.** Mining process at Talvivaara.

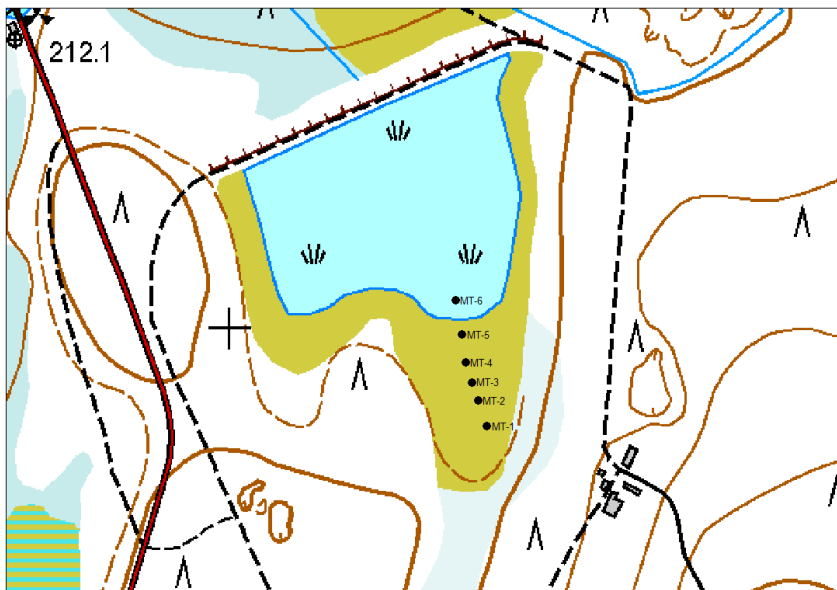
### 3 SAMPLING AND ANALYTICAL METHODS

In this section, a summary of the sampling, sample preparation and analytical methods is given. More detailed information can be found in Articles II-IV.

#### 3.1 SAMPLING

##### 3.1.1 1 SOKLI SITE

At Sokli, the aim of the study was to examine the mobilization of radionuclides and heavy metals from the mill tailings in order to assess the potential environmental impact of past and future mining activities. Samples of apatite ore and mill tailings were collected in 2010 (Article II). Ore samples were collected within the former mining area from nine piles consisting of apatite ore that had been mixed and crushed during processing. Samples of mill tailings were collected from a tailings pond near the concentration facility at the northern edge of the tailings site (Fig. 8). Two samples were taken from each location: one from the surface and the other from 30 – 50 cm below the ground surface, except for one sampling point where only a surface sample was obtainable. The sampling transect was approximately 200 m long and the distance between sampling points 30-40 m.

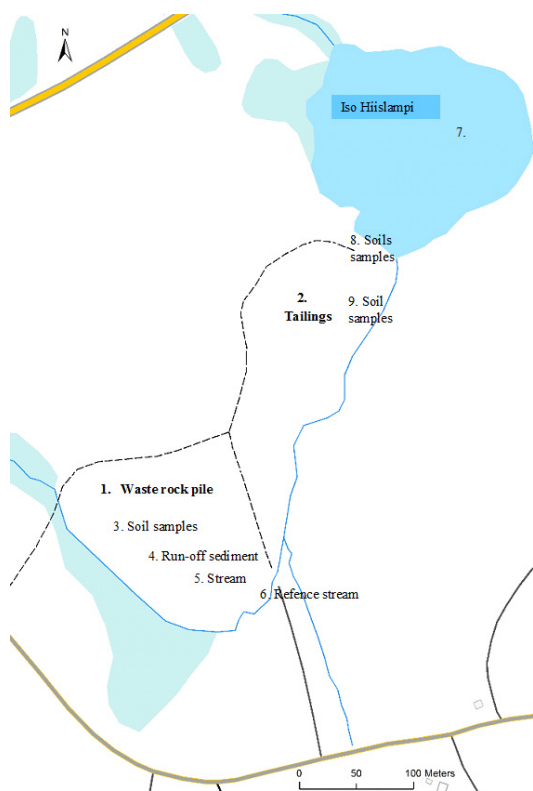


**Figure 8.** Sample locations of the mill tailings collected from six sampling points through the slurry field towards a pond at the northern edge of the tailings site



### 3.1.2 PAUKKAJANVAARA SITE

The primary aim of the study at Paukkajanvaara was to study the release of radionuclides from two sources at the site, the waste rock pile and the mill tailings (Article III). Samples from the site were collected in autumn 2010 and spring 2012 (Fig. 9). To study the releases from the waste rock pile (point 1), soil samples (point 3) and run-off sediment samples (point 4) were taken from its southeastern edge where a small stream (point 5) started, being a discharge pathway for aqueous releases from the pile. Water samples were collected from this stream, which combines to another stream (point 6), not affected by the waste rock pile, and flows to Lake Iso Hiislampi (point 7), a small lake adjacent to the site. Both water and sediment samples were collected from the lake. The mill tailings (point 2) can leach to both Lake Iso Hiislampi and the stream flowing on its eastern side. Therefore, soil samples (point 8) were taken between the tailings and the lake and between the tailings and the stream (point 9). In addition, samples from the actual mill tailings were taken.



**Figure 9.** Sampling points at the former Paukkajanvaara uranium mine area

### 3.1.3 TALVIVAARA SITE

The study at Talvivaara was focused on the behaviour of uranium and its radiotoxic daughters  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in the bioheap leaching process (Article IV). Samples were collected from the primary leaching heaps, the secondary heaps, the pregnant leach solution (PLS) ponds and the gypsum pond in 2011, 2012 and 2013. The solid samples were taken from four different leaching heaps as well as from the agglomerated ore and gypsum pond tailings. Two samples of black schist ore were taken by the Geological Survey of Finland from drill core DDKS-010 of the Kolmisoppi orebody in 2010. Four liquid samples were collected from the PLS ponds. Each PLS pond is linked to the corresponding leaching heap. Two parallel samples were taken from each sampling point. Three samples from solutions of the gypsum pond were also picked.

## 3.2 SAMPLE PRETREATMENT

The lake sediment samples collected from Paukkajanvaara were dried using a vacuum drier Christ Alpha 1-4 LSC. Other solid samples from the three sites were dried at 40°C and the samples containing organic matter at 60 °C for one week. They were sieved with 2 mm sieve except for the samples that were already of a sufficiently small grain size (<2 mm). Ore samples were ground to fine powder using a Mixer Mill Type MM-2. Water samples from Paukkajanvaara were filtered with a 0.45 µm polypropene filter straight on site to pre-treated tubes containing 0.05 ml concentrated nitric acid.

## 3.3 ANALYTICAL TECHNIQUES

### 3.3.1 X-RAY FLUORESCENCE

Portable XRF was employed on Sokli samples without pre-treatment to estimate the bulk composition and thorium content of the material on site. Analysis was carried out using a hand-held Thermo Scientific Niton XL3t 800 spectrometer in soil calibration mode. This instrument employs a miniature X-ray tube for excitation with a high-performance, solid-state Si-PIN detector.

### 3.3.2 X-RAY DIFFRACTION

Selected solid samples from Sokli and Talvivaara were analyzed with XRD to identify, semi-quantitatively, the main minerals present. Analyses were performed using a

Philips X'Pert MPD diffractometer. The X-ray diffraction spectra were recorded from 2-70° 2θ (step size 0.02 °θ, time per step 1.00 s). The minerals were identified with PANalytical X'Pert HighScore Plus software using the ICDD pdf-4/minerals database.

### 3.3.3 ELECTRON PROBE MICRO-ANALYSIS

Electron probe micro-analysis was applied for selected solid samples from Sokli and Talvivaara to identify the uranium- and thorium-bearing minerals. Analyses were performed by wavelength-dispersive spectroscopy using a Cameca SX100 instrument at the Geological Survey of Finland, Espoo. Analyzing conditions were as follows: accelerating voltage 15 kV and beam current and diameter 10 nA and 1-5 micrometers, respectively. Natural minerals and metals were employed as standards. Analytical results were corrected using the PAP on-line correction program.

### 3.3.4 GAMMA SPECTROMETRY

Gamma spectrometry was used for estimation of natural uranium and thorium series isotopes from dried solid samples.  $^{238}\text{U}$  was measured with the aid of gamma emission of the progeny nuclide  $^{234\text{m}}\text{Pa}$  in equilibrium with  $^{238}\text{U}$ . Correspondingly,  $^{228}\text{Ra}$  was obtained from its daughter  $^{228}\text{Ac}$  (Beddow et al. 2006).  $^{226}\text{Ra}$  was determined directly from the emission with the aid of the progeny nuclides  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$ , assumed to be in secular equilibrium with their progenitor.  $^{228}\text{Th}$  was determined using progeny nuclides  $^{208}\text{Tl}$  and  $^{212}\text{Pb}$ .  $^{232}\text{Th}$  was estimated from  $^{228}\text{Ac}$ , assuming secular equilibrium with  $^{228}\text{Ra}$ , though the assumption is tentative (Read et al. 2013). In order to prevent the escape of radon and thus ensure the attainment of radioactive equilibrium between  $^{226}\text{Ra}$  and  $^{214}\text{Pb}/^{214}\text{Bi}$ , as well as between  $^{228}\text{Th}$  and  $^{208}\text{Tl}/^{212}\text{Pb}$ , the samples were sealed in vacuum bags for three weeks. The samples were counted on a Canberra BE5030 HPGe detector with cryostatic cooling and Gemini auto-sampling. Prior to analysis, the detector was calibrated with a mixed nuclide standard (NPL) of similar geometry and density (washed sand, Thermo Fisher). The spectra were analyzed using the Gamma99 spectral analysis software.

### 3.3.5 SAMPLE DIGESTION EXPERIMENTS

Sample digestion experiments were performed to optimize the method for microwave digestion, allowing determination of uranium and thorium by ICP-MS

and uranium, thorium,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  by alpha spectrometry. These experiments were made using two ore samples and one mill tailing sample from both Sokli and Talvivaara. Powdered samples were weighed into pre-cleaned vessels and various acid combinations were added. The effect of the sample mass on the digestion efficiency was also tested with one sample from both sites. Increasing masses of sample were weighed into the vessel, acid combinations were added and finally the samples were dissolved using microwave digestion. After cooling, the digests were filtered with a  $0.45\ \mu\text{m}$  polypropylene filter.

### **3.3.6 INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY**

Elemental compositions of all the samples were determined by Agilent 7500 ce/cx Inductively Coupled Plasma Mass Spectrometer (ICP-MS), in the case of the solid samples after microwave digestion. The resulting spectra were analysed using the Masshunter spectral analysis software. Elemental standard solutions were prepared by diluting single-element standard solutions (Merck), diluted with 5%  $\text{HNO}_3$ . Water used in preparation of dilute nitric acid was purified using a Milli-Q water purification system (Millipore, USA).

### **3.3.7 ALPHA SPECTROMETRY**

To determine uranium and thorium isotopes by alpha spectrometry, they were separated from microwave digests using anion exchange chromatography: uranium was first separated in 9M HCl and then thorium in 8M  $\text{HNO}_3$  (Juntunen et al. 2001). The radiotracers used for determination of chemical yield in uranium and thorium separations were  $^{236}\text{U}$  and  $^{229}\text{Th}$ , respectively. For samples collected from Talvivaara,  $^{210}\text{Po}$  was separated by spontaneous precipitation on silver discs and measured by alpha spectrometry and  $^{210}\text{Pb}$  was precipitated from the remaining solution. After half a year, the new ingrowth of  $^{210}\text{Po}$  was again separated by spontaneous deposition measured by alpha spectrometry, which represents the initial  $^{210}\text{Pb}$  activity in the sample. The alpha spectrometric measurements were performed with PIPS semiconductor detectors of  $600\ \text{mm}^2$  active area, housed in Alpha Analyst model 7200-08.

### **3.3.8 SEQUENTIAL EXTRACTIONS**

A two-step sequential extraction was performed to selected Sokli samples in order to study the geochemical association of metals and radionuclides in the ores and mill

tailings. Three samples of both the ore and mill tailings were taken. To determine the metal content, one sample from each extraction was analysed by ICP-MS. The steps and the targeted forms were as follows:

**Fraction 1. Exchangeable.** The first step was carried out using  $\text{NH}_4\text{Cl}$ . In this step, 30 mL of 1 M  $\text{NH}_4\text{Cl}$  at pH 5.5 was added to 2 g of the solid sample. The mixture was shaken for 1 h at room temperature. The solution was then separated from the solid sample by centrifugation at 7500 rpm for 15 min and filtered to 0.25  $\mu\text{m}$  (polyethersulfone PES, Nalgene; Thermo Fisher Scientific, Waltham, MA, USA). The sample was washed twice with 30  $\text{cm}^3$  of the reagent, centrifuged and the washings added to the extracted solution.

**Fraction 2. Desorbable in mild acids.** In the second step, the residual solid sample from the first extraction was treated with 1 M  $\text{CH}_3\text{COONH}_4$  (in 25%  $\text{CH}_3\text{COOH}$ ) at pH 4.5, for 2 h at 50°C. The centrifugation and washing were performed as for fraction 1 and again the washings were added to the extracted solution.

## 4 RESULTS AND DISCUSSION

### 4.1 COMPARISON OF THE ANALYTICAL METHODS FOR DETERMINING URANIUM AND THORIUM IN ORES AND MILL TAILINGS (ARTICLE I)

In order to assess the environmental impact of the radionuclides released, site characterization usually requires a large number of samples. The aim of this study was to find an efficient and reliable procedure for the determination of uranium and thorium in ores and mill tailings. First, a portable XRF analyser was used to obtain an estimate of the uranium and thorium content on site. Then, in the laboratory, the activity concentrations of uranium and thorium in solid samples were measured using gamma spectrometry. The mineral composition was determined by XRD and uranium and thorium-bearing minerals were identified by EPMA. Thereafter, to determine the uranium and thorium contents by ICP-MS and alpha spectrometry, microwave digestion was performed with the most commonly used mineral acids, alone and in combination, and with varying sample masses.

In the case of Sokli, two ore samples (S-O-1, S-O-9) and one mill tailings sample (S-MT-3) were selected for the study. The uranium-bearing minerals in sample S-O-1 are pyrochlore  $[(\text{Na,Ca})_2\text{Nb}_2\text{O}_6(\text{OH,F})]$  and monazite  $[(\text{Ce,L a,Nd,Th})\text{PO}_4]$ . The results showed (Table 1) that digestion with nitric acid with/without addition of HF was the most effective for this sample. Uranium in the mill tailings sample S-MT-3 is incorporated in pyrochlore and monazite, as in sample S-O-1, which suggests a similar digestion efficiency for both samples. This was found to be the case; the most efficient agent was found to be nitric acid. However, unlike sample S-O-1, addition of HF to sample S-MT-3 gave slightly lower results compared to pure nitric acid, which might be caused by different partitioning of uranium between monazite and pyrochlore in the sample; if most of the uranium is bound in pyrochlore, which already has fluoride in its lattice, strong complexation with fluoride in HF solution might be hindered. For sample S-O-9, aqua regia and nitric acid were the most effective agents. In contrast to S-O-1 and S-MT-3, monazite was not encountered in the S-O-9 ore sample, but uranium is mainly bound in pyrochlore. Pyrochlore contains fluoride, as noted previously, which is probably the reason why HF addition did not increase the solubility. The use of aqua regia yielded slightly higher uranium concentrations than nitric acid.

In addition to the pyrochlore-group minerals, high thorium contents were also identified by electron probe micro-analyses in cheralite  $(\text{Ca,Ce,Th})(\text{P,Si})\text{O}_4$  from

Sokli. Nitric acid was found to be the most efficient thorium-digesting agent for every sample. Aqua regia gave the second best results, mostly because of the presence of nitric acid; addition of hydrochloric acid did not enhance the thorium solubility, since thorium does not form a negative chloride complex. Where HF was present, the digestion efficiency was poorer, which is probably due to fluoride in thorium-bearing pyrochlore and thorium precipitation with fluoride. In conclusion, dissolution of thorium as a nitrate complex is the most efficient.

Three samples from Talvivaara were also selected for the study: two ore samples (T-O-F, T-O-L) and one gypsum pond sample (T-T-1). In the agglomerated, unleached Talvivaara ore sample T-O-F, uranium is mainly bound in uraninite, which is principally enclosed in carbonaceous nodules. Small amounts of uranium were also found in monazite and xenotime ( $\text{YPO}_4$ ), whereas thorium is mostly bound in uraninite. Nitric acid was found to be the most efficient digestion agent for extraction of uranium from the untreated sample. In the leached ore sample T-O-L, most of the uranium has already been removed in the heap-leaching process on site. Addition of HF in nitric acid improved extraction of the remaining uranium from this sample. This might be due to leaching primarily from the carbonaceous nodules; if the residual uranium were bound in monazite, the addition of HF would have improved the extraction results, as mentioned above in the case of the Sokli samples. Uranium in the gypsum pond tailings occurs in association with goethite but only one goethite grain was analysed by EPMA. Extraction of uranium from these samples with aqua regia gave a solution with 110 ppm U whereas addition of HF slightly improved the extraction to 116 ppm. As with the Sokli samples, separation of thorium as a nitrate complex was found to be the most efficient for every sample.

Based on all the results presented in Table 1, a conclusion can be made that pure nitric acid is the most efficient medium for leaching thorium from all of the studied samples. It also performs better than the other reagents for leaching uranium from most of the samples. The other acid digestions gave a 59% yield compared to pure nitric acid. On average, the thorium digestion yield of other acids was 37% compared to pure nitric acid, with the range being very wide, from 0 to 78%. The corresponding values for uranium were 81% (average) and 45-120% (range). Selection of the most appropriate digestion method is clearly more critical in the case of thorium than uranium.

**Table 1.** Performance of various acid digestions in leaching of uranium and thorium from ore and mill tailings samples from Sokli and Talvivaara. For HNO<sub>3</sub> digestions, the values represent the observed U and Th concentrations (ppm) in the ores and mill tailings, respectively, whereas for the other acids, the values are relative values (%) compared to HNO<sub>3</sub> digestions.

Sample code	HCl + HNO <sub>3</sub>		HNO <sub>3</sub> + HCl + HF		HCl + HNO <sub>3</sub> + HF		HNO <sub>3</sub> + HF		HNO <sub>3</sub>	
	U	Th	U	Th	U	Th	U	Th	U	Th
S-O-1	45%	78%	86%	< LOD*	-	-	109%	< LOD	66 ppm	203 ppm
S-O-9	109%	50%	63%	46%	-	-	72%	63%	54 ppm	252 ppm
S-MT-3	48%	47%	57%	18%	-	-	68%	57%	90 ppm	201 ppm
T-O-L	80%	71%	70%	14%	90%	71%	120%	43%	10 ppm	7 ppm
T-O-F	60%	64%	64%	18%	68%	64%	80%	27%	25 ppm	11 ppm
T-T-1	109%	25%	115%	1%	87%	0.3%	97%	4%	101 ppm	4 ppm

\* LOD – under the limit of detection.

After the sample digestion experiments, the effect of sample mass on the digestion efficiency was tested with one sample both from Sokli and Talvivaara. Increasing masses of sample (0.1–2.0 g from Talvivaara and 0.1–2.5 g from Sokli for digestion with concentrated nitric acid, 0.5–2.0 g from Talvivaara and 1.0–2.5 g from Sokli with other acid combinations described in Table 1) were weighed into the vessel, acid combinations were added, and finally the samples dissolved by microwave digestion. Since nitric acid gave the best extraction, it was used to lower sample masses from 0.1 g to 0.5 g in the experiments. The variation of the element concentration as a function of the sample mass was not significant, taking into account the inhomogeneous nature of the used environmental samples.

Following the sample digestion experiments, comparison of the concentration measurement methods (ICP-MS, gamma spectrometry, alpha spectrometry, XRF for Sokli samples) used in the further studies of the sites was made (Table 2). All the samples from Talvivaara and Sokli were analysed by ICP-MS for their uranium and thorium concentrations, for which 0.5 g subsamples were microwave-digested using nitric acid. For alpha spectrometry, uranium and thorium were separated using anion exchange chromatography from the same digestion solution used for ICP-MS analysis. Gamma spectrometry was applied to dried, untreated samples. XRF was employed for the Sokli samples to determine the thorium contents and major element compositions on site; uranium concentrations were below the detection limit (40 ppm without pre-treatment). Uranium concentrations obtained by alpha and gamma spectrometry were close to each other. The ratio of gamma to alpha spectrometry results was  $1.05 \pm 0.21$  on average. In most cases, gamma and alpha spectrometry gave slightly lower uranium concentrations than ICP-MS; the ratio of gamma spectrometry to ICP-MS results was  $0.87 \pm 0.23$  and the ratio of alpha spectrometry to ICP-MS results  $0.85 \pm 0.20$ . According to Kaste et al. (2006),



<sup>234m</sup>Pa has a low yield of gamma emission at 1001 keV because of the low emission probability and detector efficiencies in this energy region, which may be the cause of the lower concentrations observed by gamma spectrometry. For alpha spectrometry, the limited precision due to counting statistics may cause the slightly lower results. However, considering the uncertainty limits in each method, the correspondence of the results is good for most of the samples.

**Table 2.** Mean uranium concentrations determined using gamma spectrometry and alpha spectrometry relative to the concentrations measured with ICP-MS and the ratio of gamma to alpha spectrometry.

	Mean ratio	Standard deviation
Gamma spectrometry / ICP-MS	0.87	0.23
Alpha spectrometry / ICP-MS	0.85	0.20
Gamma spectrometry/ Alpha spectrometry	1.05	0.21

On average, the lowest thorium concentrations were obtained by ICP-MS (Table 3). The average ratio of gamma spectrometry to ICP-MS results was  $1.07 \pm 0.45$ , alpha spectrometry to ICP-MS results  $1.20 \pm 0.40$  and XRF to ICP-MS results  $1.10 \pm 0.50$ . Since ICP-MS gave systematically lower thorium concentrations than alpha and gamma spectrometry, it can be concluded that ICP-MS results are indeed lower due to challenges in the sample preparation and thorium measurement.

**Table 3.** Mean thorium concentrations determined using gamma spectrometry, alpha spectrometry and XRF relative to the concentration measured with ICP-MS.

	Mean ratio	Standard deviation
Gamma spectrometry / ICP-MS	1.07	0.45
Alpha spectrometry / ICP-MS	1.20	0.40
XRF / ICP-MS	1.10	0.50

ICP-MS, alpha and gamma spectrometry are all suited to the determination of uranium and gave broadly similar results. In addition, alpha spectrometry also offers the possibility of obtaining isotopic information to determine the activity concentrations of isotopes in environmental samples. Interestingly, portable XRF also gave comparable results when used on site despite the fact that the measurements were made on raw unprepared specimens rather than on beads or pressed powders. Pre-screening of a large number of samples in situ by XRF followed by subsequent calibration against more sensitive methods on fewer samples may be the most promising compromise between analytical accuracy and representative site coverage.

## 4.2 RADIONUCLIDE AND HEAVY METAL REDISTRIBUTION AT THE FORMER PILOT-SCALE APATITE PLANT AT SOKLI, NORTHERN FINLAND (ARTICLE II)

The aim of the study at Sokli was to examine the mobility of radionuclides from the mill tailings over the forty years since the Sokli concentration plant ceased operation. This was done in order to assess the likely environmental consequences of any future activities for beneficiation of the phosphate ore. First, the main minerals of the samples collected from Sokli were determined by XRD. The main minerals and the percentages in the phosphate ore are: apatite ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ), 75%; goethite ( $\text{FeO}(\text{OH})$ ), 10%; vermiculite ( $(\text{Mg,Fe,Al})_3(\text{Al,Si})_4\text{O}_{10}(\text{OH})_2$ ), 8%; and magnetite ( $\text{Fe}_3\text{O}_4$ ), <5%. In one of the samples, dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) was also found with an abundance of <5%. In the mill tailings, the main minerals are: apatite, 73%; plagioclase ( $(\text{Ca,Na})\text{Al}_2\text{Si}_2\text{O}_8$ ), 13%; quartz, 10%; and magnetite, 3%. One of the three samples also contained 10% of goethite and less than 5% of vermiculite, iron columbite ( $\text{FeNb}_2\text{O}_6$ ) and pyrochlore ( $(\text{Ca,Na})_2\text{Nb}_2\text{O}_6(\text{OH,F})$ ). The fact that the apatite content in the mill tailings is almost the same as in the parent ore revealed that the physical concentration process performed failed to extract significant apatite and therefore, the mill tailings do not represent the composition that would be obtained in an optimized full-scale beneficiation process.

Quantitative chemical analyses of uranium- and thorium-bearing minerals were determined by electron microprobe analysis. The identified phases comprise pyrochlore (pyrochlore, bariopyrochlore, thoriopyrochlore and uranpyrochlore) and monazite group (monazite and cheralite) minerals. The highest thorium content was found in cheralite (up to 41.6%  $\text{ThO}_2$ ), whereas in pyrochlore, the  $\text{ThO}_2$  contents varied between 0.5 and 12.0 wt%. The highest uranium content was observed in uranpyrochlore (4.0 wt%  $\text{UO}_2$ ); the  $\text{UO}_2$  content in cheralite varied between 0.9 and 1.3 wt%. The crystal form is euhedral to subhedral suggesting that no or little leaching has taken place. According to the thermal neutron-induced fission track studies by Rehtijärvi and Lindqvist (1978), uranium is also bound in apatite, fine-grained goethite, and altered magnetite. In our study, however, the detection limit for uranium (0.2 wt%  $\text{UO}_2$  by microprobe analysis) was too high to quantify the uranium content in these phases. Nevertheless, it can be assumed that in addition to the pyrochlore and monazite group minerals, apatite is a significant host for uranium.

All samples were analysed by gamma spectrometry to determine activity concentrations of  $^{238}\text{U}$  and  $^{232}\text{Th}$  progeny (Table 4). Uranium and thorium were also determined by ICP-MS. The mean uranium concentration of the ore, measured by ICP-MS, was 41 ppm (range 24 - 52 ppm); the mean thorium concentration was 104 ppm (range 54 - 157 ppm). The corresponding values in the mill tailings were 65 ppm (range 39-86 ppm) and 171 ppm (range 85-248 ppm), respectively. Gamma

spectrometry gave statistically identical uranium concentrations for  $^{238}\text{U}$ : the mean ratio of uranium concentration measured by gamma spectrometry to that measured by ICP-MS was  $0.97 \pm 0.13$ . The corresponding ratio for the determination of  $^{232}\text{Th}$  with these two methods was  $1.15 \pm 0.27$ . No fractionation between  $^{238}\text{U}$  and  $^{226}\text{Ra}$  can be seen, within analytical uncertainty as both are enriched to a similar degree in the mill tailings.

**Table 4.** Mean activity concentrations (Bq/kg) of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and selected progeny nuclides in Sokli ore and mill tailings measured by gamma spectrometry ( $\pm 5\%$  uncertainty).

Nuclide	$^{238}\text{U}$	$^{226}\text{Ra}$	$^{232}\text{Th}$	$^{228}\text{Th}$	$^{228}\text{Ra}$
Ore (n = 9)					
Mean	483	414	659	734	665
Range	356-670	336-606	450-724	458-859	455-733
Mill tailings (n = 11)					
Mean	730	686	677	778	682
Range	466-996	437-891	406-931	478-1081	408-936
Ratio: mill tailings/ore	1.51	1.66	1.03	1.06	1.03

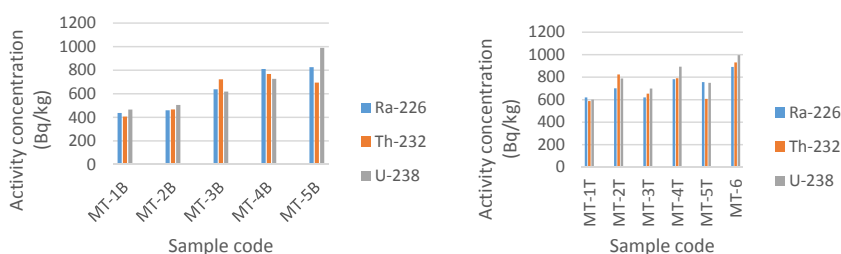
Three ore and four mill tailings samples were analysed for their uranium and thorium isotopes by alpha spectrometry, after separation by anion exchange chromatography. The nuclides determined were:  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{230}\text{Th}$ , and  $^{228}\text{Th}$  (Table 5). The isotopic ratios of  $^{234}\text{U}/^{238}\text{U}$  and  $^{228}\text{Th}/^{232}\text{Th}$  are close to unity, indicating secular equilibrium in both the ore and mill tailings. However,  $^{230}\text{Th}/^{238}\text{U}$  and  $^{230}\text{Th}/^{234}\text{U}$  ratios are clearly elevated, at about  $1.5 \pm 0.2$ , in all ore samples, which indicates that uranium has partly been mobilized from the ore. In the mill tailings, these ratios varied between 1 and 3 but no systematic differences could be seen.

**Table 5.** Isotopic ratios of  $^{234}\text{U}/^{238}\text{U}$ ,  $^{230}\text{Th}/^{238}\text{U}$ ,  $^{230}\text{Th}/^{234}\text{U}$  and  $^{228}\text{Th}/^{232}\text{Th}$  in the ore (O) and mill tailings (MT) samples.

Isotopic ratio	O-1	O-5	O-9	MT-1B	MT-1T	MT-5B	MT-6
U-234/U-238	0.99	0.99	1.01	0.89	1.03	1.00	1.03
Th-230/U-238	1.65	1.43	1.45	2.93	1.62	1.00	1.50
Th-230/U-234	1.66	1.45	1.42	3.28	1.58	1.00	1.46
Th-228/Th-232	0.91	1.00	0.91	1.03	0.99	0.94	1.03

Figure 10 presents surface/subsurface activity concentrations for uranium, radium and thorium isotopes. In both the surface and subsurface layers, the activity

concentrations increase when approaching the pond at the end of the sludge field.  $^{226}\text{Ra}$  increases laterally from 437 Bq/kg to 825 Bq/kg in the subsurface samples, but in surface samples, the variation is random from 620 Bq/kg to 891 Bq/kg. In the case of  $^{232}\text{Th}$ , the activity levels also increase laterally in the subsurface samples from 406 Bq/kg to 695 Bq/kg with the highest activity concentration being 768 Bq/kg in sample MT-4B. In the surface samples, the activity concentrations vary from 588 Bq/kg to 930 Bq/kg, but no systematic trend can be seen. The activity concentration of  $^{238}\text{U}$  increases in the subsurface samples laterally from 466 Bq/kg to 995 Bq/kg and in the surface samples the variation is again random, ranging from 600 Bq/kg to 995 Bq/kg.



**Figure 10.** Activity concentrations (Bq/kg) of radium, thorium and uranium isotopes in the surface (a) and subsurface (b) samples taken from Sokli mill tailings along a 200 m transect.

There is no clear evidence for vertical migration of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{238}\text{U}$  through the profile, as evidenced by the randomness of their distribution and positive correlation of isotopic activity concentrations in the surface samples for these nuclides. The positive correlation between  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{238}\text{U}$  activity concentrations can also be seen in the subsurface samples. Therefore, the reason for the variation in the activity concentrations across the site is a compositional change in material discharges rather than subsequent mobilization.

Sequential extractions were performed to determine the potential mobility of uranium and thorium.  $\text{NH}_4\text{Cl}$  was used to extract elements that are bound by weak electrostatic forces to mineral and organic matter surfaces. The exchangeable fractions of uranium were on average 0.01% in both ore and mill tailings. The corresponding values for thorium were 0.01% in the ore and 0.004% in the mill tailings.

1 M  $\text{CH}_3\text{COONH}_4$  (in 25%  $\text{CH}_3\text{COOH}$ ) was used to determine uranium and thorium that are soluble under weakly acidic conditions. This fraction was described as ‘desorbable in mild acid’. The average concentration of thorium in the ore is the same as in the exchangeable fractions (0.04%), implying that thorium is tightly bound in mineral phases. Desorbable uranium was clearly higher (4%) than the exchangeable fraction. The weakly acidic conditions promote the oxidation of

tetravalent uranium to the hexavalent form, increasing the solubility of uranium (Lehto and Hou 2011).

At present, the Sokli mining site has had only a limited impact on the surrounding area. Based on positive correlation between uranium, radium and thorium in the tailings, variations in abundance probably represent material discharges to the tailings rather than mobilization of the elements from the tailings themselves. Similarly, no indication of heavy metal migration was found. Most of the elements are tightly bound to the sample matrix and therefore not easily released, suggesting limited impact on local waters to date.

#### **4.3 RELEASE OF RADIONUCLIDES FROM WASTE ROCK AND MILL TAILINGS AT A FORMER URANIUM MINE IN EASTERN FINLAND**

A critical evaluation of the mine remediation techniques is essential for determining their effectiveness and the long term impact on the surrounding environment. This requires post-implementation data from samples taken well after the mine closure (Lottermoser and Ashley 2005). The aim of this study was to examine the potential for further mobilization of radionuclides from the tailings and waste rock pile at Paukkajanvaara some fifteen years after the remedial action was completed. As mentioned in section 3.1.2, there are two primary contamination sources at the site: the waste rock pile and tailings deposit. To study the releases from the waste rock pile, soil samples and run-off sediment samples were collected from its southeastern edge as well as water samples from a stream being the discharge pathway for aqueous releases from the pile. The results from five soil profiles taken from the south-eastern edge of the waste rock pile are presented in Table 6. The Riutta area, which is situated 12 km from Paukkajanvaara and resembles it in its nature and geology, was used by the Finnish Radiation and Nuclear Authority as a reference site of Paukkajanvaara (Mustonen et al. 1989). The concentration of  $^{226}\text{Ra}$  at Riutta is approximately five times lower than at Paukkajanvaara (Table 6). The concentration of  $^{226}\text{Ra}$  is also 20 times higher at Paukkajanvaara compared to the average concentrations in Finland. The concentration of  $^{238}\text{U}$  resembles the concentration at Riutta on average, but is 10 times higher than the average concentrations in Finland (Lemmelä 1984).

**Table 6.** Average concentrations of  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$  and  $^{238}\text{U}$  (Bq/g) in five soil samples taken from the south-eastern edge of the waste rock pile at Paukkajanvaara compared with average concentrations at the Riutta reference site and Finland.

<b>Litter</b>	<b>Activity Concentration (Bq/g)</b>		
	$^{210}\text{Pb}$	$^{226}\text{Ra}$	$^{238}\text{U}$
Range	0.6–1.9	0.4–3.4	0.5–1.4
Average	1.1	2	1.0
<b>Humus</b>	<b>Activity Concentration (Bq/g)</b>		
	$^{210}\text{Pb}$	$^{226}\text{Ra}$	$^{238}\text{U}$
Range	0.4–1.1	1.1–2.3	0.6–1.3
Average	0.7	1.7	0.9
<b>Mineral layer</b>	<b>Activity Concentration (Bq/g)</b>		
	$^{210}\text{Pb}$	$^{226}\text{Ra}$	$^{238}\text{U}$
Range	0.2–0.9	0.3–1.7	0.3–0.8
Average	0.5	0.8	0.4
<b>Riutta</b>	<b>Activity Concentration (Bq/g)</b>		
	$^{210}\text{Pb}$	$^{226}\text{Ra}$	$^{238}\text{U}$
Range	-	0.2–0.3	0.1–0.8
<b>Finland</b>	<b>Activity Concentration (Bq/g)</b>		
	$^{210}\text{Pb}$	$^{226}\text{Ra}$	$^{238}\text{U}$
Range	-	0.03–0.06	0.03–0.06

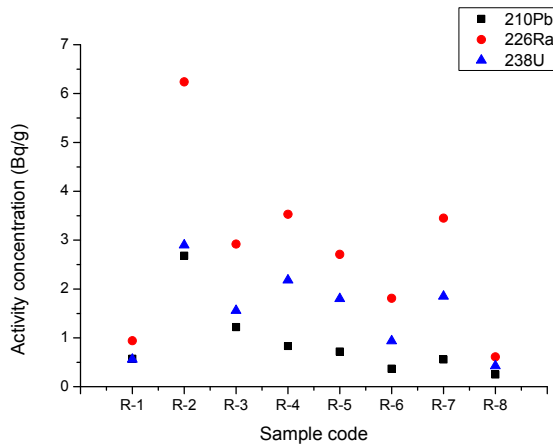
Table 7 presents the isotopic ratios of  $^{226}\text{Ra}/^{238}\text{U}$  and  $^{210}\text{Pb}/^{226}\text{Ra}$  in the five soil samples. The average  $^{226}\text{Ra}/^{238}\text{U}$  ratio in the three soil layers ranges from 1.9 to 2.6, suggesting that  $^{226}\text{Ra}$  has been preferentially leached from the pile and deposited in the surrounding soil. The  $^{210}\text{Pb}/^{226}\text{Ra}$  ratio ranges from 0.43 to 0.52, which can be attributed to incomplete ingrowth of  $^{210}\text{Pb}$ .

**Table 7.** Isotopic ratios of  $^{226}\text{Ra}/^{238}\text{U}$  and  $^{210}\text{Pb}/^{226}\text{Ra}$  in five soil samples taken from the southeastern edge of the waste rock pile at Paukkajanvaara.

	Litter		Humus		Mineral layers	
	$^{226}\text{Ra}/^{238}\text{U}$	$^{210}\text{Pb}/^{226}\text{Ra}$	$^{226}\text{Ra}/^{238}\text{U}$	$^{210}\text{Pb}/^{226}\text{Ra}$	$^{226}\text{Ra}/^{238}\text{U}$	$^{210}\text{Pb}/^{226}\text{Ra}$
Range	2.2 – 3.2	0.45 – 0.56	1.83 – 1.91	0.40 – 0.45	2.1 – 3.0	0.35 – 0.53
Average	2.6	0.52	1.87	0.43	2.5	0.44
Standard deviation	0.5	0.04	0.04	0.04	0.4	0.09

The run-off sediment samples were taken at 10 m intervals from a dry stream bed near the waste rock pile, starting from the beginning of the stream (between points 4 and 5, Fig. 9). Figure 11 presents the activity concentrations of  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$

and  $^{238}\text{U}$  in the run-off sediment samples measured by gamma spectrometry. The values are higher compared to the values determined from the soil samples taken from the south-eastern edge of the waste rock pile. The concentrations are highest after 10 m from the start of the stream and decrease along the flow direction. At points R-1 and R-8,  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$  and  $^{238}\text{U}$  are in secular equilibrium. Between these points,  $^{238}\text{U}$  and  $^{226}\text{Ra}$  are enriched.



**Figure 11.** Activity concentrations (Bq/g) of  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$  and  $^{238}\text{U}$  in run-off sediment samples taken from a dry stream bed near the waste rock pile at Paukkajanvaara.

Six water samples were collected from a stream (Fig. 12) crossing the Paukkajanvaara mine site to determine possible leaching of uranium from the waste rock pile. Samples were collected between the run-off sediment sampling area towards the mill tailings (between points 4 and 2, Fig. 9). Two reference samples were also collected; one from a small pond just outside the mining area (reference 1) and the other from a stream also crossing the Paukkajanvaara site, but without connection to the waste rock pile (reference 2). The results are presented in Table 8. Elevated uranium concentrations (2-9 ppb) in water samples were detected. The concentration of thorium varied randomly and no systematic behaviour along the stream path could be seen. The concentrations of uranium greatly exceed the average concentrations in the streams in Finland (Tenhola and Tarvainen 2008). However, the uranium concentration is lower on average in the stream compared to the reference stream assumed to have not been affected by the waste rock pile.

**Table 8.** Concentrations (ppb) of uranium and thorium in stream water samples collected between the run-off sediment sampling site and mill tailings repository ( $n=6$ ) at Paukkajanvaara.

	U	Th
range	2 - 9	0.02 - 0.06
average	4	0.03
standard deviation	3	0.02
Reference 1.	7	0.04
Reference 2.	8	0.06
Concentration range in Finland	0.07 - 0.21	n.a

To study the release of radionuclides from the tailings repository, three tailings core samples from variable depths, soil samples and water samples were collected. Table 9 presents the isotopic ratios of  $^{238}\text{U}/^{226}\text{Ra}$  and  $^{226}\text{Ra}/^{210}\text{Pb}$  of the tailings samples measured by gamma spectrometry. The samples consist of sandy tailings with the exception of sample MT-1, where an organic layer of  $\sim 3$  cm thickness occur at a depth of 4 m; this possibly represent the peat on top of which the tailings were placed. For  $^{238}\text{U}$  and  $^{226}\text{Ra}$ , the highest concentrations were observed in sample MT-1 from this organic layer, 36 Bq/g and 30 Bq/g, respectively.  $^{210}\text{Pb}$  could not be detected. The  $^{238}\text{U}/^{226}\text{Ra}$  ratios are close to unity in the tailings samples MT-1 and MT-2 varying from 0.88 to 1.36. Values  $<1$  would be expected, since uranium was leached from the ore using sulfuric acid, when most of the  $^{226}\text{Ra}$  commonly remains undissolved through the leaching process, and the concentration of radium in the tailings is usually only slightly less than that in the ore. This might indicate that tailings samples partly represent material which has been treated only physically without hydrometallurgical treatment. Only in sample MT-3 at depth interval 3 – 4.5 m the absence of  $^{238}\text{U}$  could be seen clearly. At a depth of 5 m, the isotopic ratio of  $^{238}\text{U}/^{226}\text{Ra}$  was 1.68; again clearly  $>1$ . This indicates vertical mobilization of  $^{226}\text{Ra}$  to deeper layers in the deposit, if the core presents true tailings. The isotopic ratio of  $^{226}\text{Ra}/^{210}\text{Pb}$  varies throughout the sampling depths from 1.1 to 2.0; all the ratios are  $>1$ , which indicates incomplete ingrowth of  $^{210}\text{Pb}$ .



**Table 9.** Radionuclide ratios of  $^{238}\text{U}/^{226}\text{Ra}$  and  $^{226}\text{Ra}/^{210}\text{Pb}$  in the mill tailings samples from Paukkajänvaara, measured by gamma spectrometry.

Sample code	Depth (m)	$^{238}\text{U}/^{226}\text{Ra}$	$^{226}\text{Ra}/^{210}\text{Pb}$
MT-1	2.5	0.93	1.62
	4	0.95	1.15
	4	1.20	-
	4.5	1.26	1.98
MT-2	3	0.88	1.52
	3.5	1.36	1.32
MT-3	3	-	-
	4	-	1.17
	4.5	-	-
	5	1.68	1.66

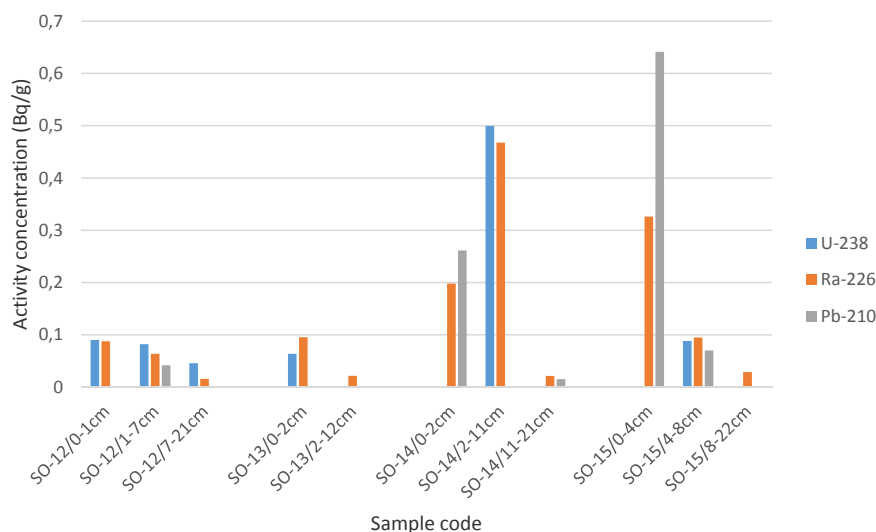
Soil samples collected between the mill tailings repository and Lake Iso Hiislampi showed no evidence of leakage of radionuclides (Table 10). As seen in Table 10, the concentrations of thorium vary in the sampled soil layers from 0.012 Bq/g to 0.024 Bq/g. In the case of uranium, the concentrations vary from 0.1 to 1.0 Bq/g. The results correspond to the values of the reference site Riutta, and therefore the release of contaminants from the tailings on this pathway seems not to be plausible.

**Table 10.** Average concentrations of uranium and thorium (Bq/g) in the six soil samples collected between Lake Iso Hiislampi and tailings area at Paukkajänvaara.

Organic layer	Concentration (Bq/g)	
	$^{238}\text{U}$	$^{232}\text{Th}$
Range	0.1–0.6	0.012–0.020
Average	0.3	0.016
Mineral layer	Concentration (Bq/g)	
	$^{238}\text{U}$	$^{232}\text{Th}$
Range	0.1–1.0	0.016–0.024
Average	0.4	0.020

Four soil samples were collected between the stream and tailings area (Fig. 12). The activity concentrations of U and its progeny in these samples are much lower than those found in five soil samples taken between the waste rock pile and run-off sediment. Moreover and in contrast to the latter, they show no enrichment in  $^{226}\text{Ra}$ . In the organic layer of sample SO-12,  $^{210}\text{Pb}$  is below the detection limit (approximately 0.01 Bq/g), which indicates incomplete ingrowth and leaching of

$^{238}\text{U}$  and  $^{226}\text{Ra}$  with the surface flow and binding to organic matter. The same can be seen in sample SO-13 in both in the organic and mineral layer. Samples SO-14 and SO-15 are enriched in  $^{210}\text{Pb}$  at the surface. This may be caused by leaching of  $^{238}\text{U}$  and  $^{226}\text{Ra}$  and/or settling of  $^{210}\text{Pb}$  after  $^{222}\text{Rn}$  decay in the atmosphere. At the subsurface (2-11 cm) in sample SO-14,  $^{238}\text{U}$  and  $^{226}\text{Ra}$  are in equilibrium.  $^{210}\text{Pb}$  could not be detected. This again suggests leaching of uranium and  $^{226}\text{Ra}$  with the surface flow and incomplete ingrowth of  $^{210}\text{Pb}$ . In addition, an increase in the uranium concentration can be seen in water samples, when the stream has passed the tailings area (app. 8 ppb). The highest concentration was determined from the sample taken from an inlet of Lake Iso Hiislampi (12 ppb). The concentrations in the water samples are again higher than the average concentrations in the streams in Finland (0.07 – 0.21 ppb). Compared to the reference stream (8 ppb), however, uranium concentrations are similar.

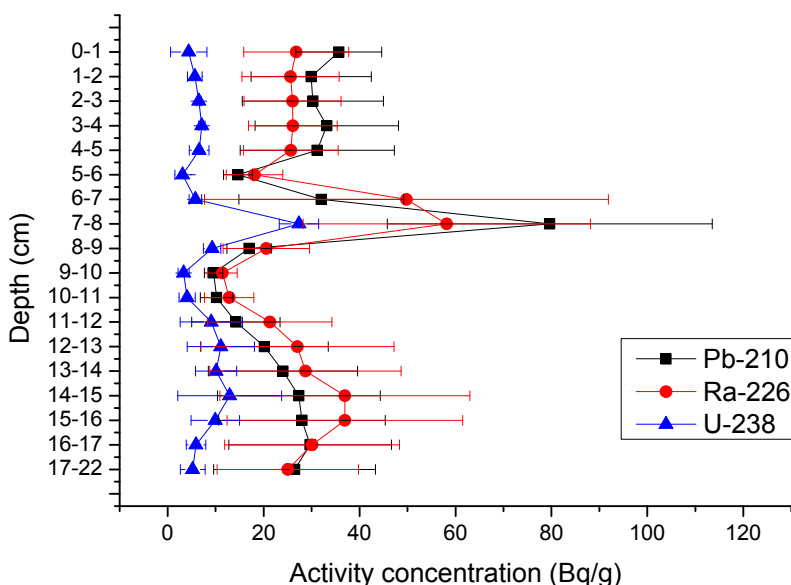


**Figure 12.** Activity concentrations (Bq/g) of  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$  and  $^{238}\text{U}$  measured by gamma spectrometry in the soil samples collected between the stream and mill tailings area at the former Paukkajanvaara mining site (uncertainty app. 7%).

The stream finally flows to Lake Iso Hiislampi, a small lake at the mine site. Three lake sediment cores were collected from the bottom of Lake Iso Hiislampi in the center of the lake and sliced into 1-cm-thick slices immediately after sampling. The sediment samples from depth interval of 6 – 22 cm, consist of either grey sludge, black organic material or a mixture of these and smell strongly of sulfur. The top 0-6 cm layers of the samples were pure organic matter. The average sedimentation rate in Finland is 1.5 – 3.5 mm per year. This means, that the first 0-6 cm were formed within 24 years assuming an average sedimentation rate of 2.5 mm per year. This

dates back to the early 1990s, the date of remediation. The Finnish Nuclear and Safety Authority concluded in its study in 1989 that the sediments from the years 1963-1964 occur at a depth of 14 – 16 cm and that the tailings started to spread to Lake Iso Hiislampi after the operation ceased (Mustonen et al. 1989). This means that the lower layers (6- 22 cm) in the samples of the study consist mainly of the tailings; this was clear from their appearance.

Figure 13 presents the average activity concentrations of  $^{238}\text{U}$ ,  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  as a function of depth. For  $^{238}\text{U}$ ,  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  a peak concentration can be seen at a depth of 7-8 cm: the concentrations are 27 Bq/g, 80 Bq/g and 58 Bq/g, respectively. In the layers at 8-22 cm, the concentrations of  $^{238}\text{U}$ ,  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$  vary from 3 – 12 Bq/g, 10 – 30 Bq/kg and 11 – 37 Bq/g, respectively. In the top layers, the concentrations are similar, varying from 30-36 Bq/g for  $^{210}\text{Pb}$ , approximately 26 Bq/g for  $^{226}\text{Ra}$  and 6-7 Bq/g for  $^{238}\text{U}$ . At the Riutta reference site, the concentrations in the top layers (0-5 cm) were approximately 0.2 Bq/g for  $^{210}\text{Pb}$ , approximately 0.2 Bq/g for  $^{226}\text{Ra}$  and 0.1 Bq/g for  $^{238}\text{U}$  (Sillanpää et al. 1989). Thus, the concentrations of the Lake Iso Hiislampi sediments are approximately 100 times higher than at Riutta.



**Figure 13.** The average activity concentrations of  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$  and  $^{238}\text{U}$  as a function of depth in three sediment samples collected from the bottom of Lake Iso Hiislampi at the Paukkanvaara mine site.

The peak concentrations in the lake sediment samples most probably represent a discharge of fine-grained tailings material to the lake, which is supported by the isotopic ratios of  $^{226}\text{Ra}/^{238}\text{U}$  ( $>1$ ). In the upper organic-rich layers of the core ( $<6$  cm), the concentrations of  $^{226}\text{Ra}$  are fairly constant and are enriched in  $^{210}\text{Pb}$ , which might be caused by the settling of  $^{210}\text{Pb}$  after  $^{222}\text{Rn}$  decay in the atmosphere,

mobilization of  $^{226}\text{Ra}$  to lower layers in the sediment profile and/or leaching of  $^{210}\text{Pb}$ . The concentrations of  $^{226}\text{Ra}$  compared to  $^{238}\text{U}$  also suggests that there is further leaching of  $^{226}\text{Ra}$  from the waste rock pile and/or tailings area.

#### 4.4 BEHAVIOR OF RADIONUCLIDES IN THE MINING PROCESS AT TALVIVAARA, EASTERN FINLAND

The Talvivaara mine in eastern Finland utilizes microbe-induced heap leaching to recover nickel and other valuable metals (Zn, Cu, Co) from black schist ore. In addition to these metals, the deposit contains uranium at an average concentration level of 17 ppm, incorporated in uraninite ( $\text{UO}_2$ ). Uranium oxidizes from the U(IV) to U(VI) state during leaching and dissolves as the uranyl ion ( $\text{UO}_2^{2+}$ ) in the acidic pregnant leach solution. The aim of this study was to generate new data leading to a better understanding of the fate of the radiotoxic daughter nuclides of uranium, primarily  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ , in the mining process.

To study the behaviour of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$ , all ore samples were measured by gamma spectrometry to determine activity concentrations of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$  in the Talvivaara heaps (Table 11).  $^{226}\text{Ra}$  activity concentrations vary from 115 Bq/kg to 222 Bq/kg within the 2.5 years leaching time whereas concentrations of  $^{228}\text{Ra}$  range from 17 Bq/kg to 27 Bq/kg. The concentrations of  $^{228}\text{Th}$  are similar (range 19 Bq/kg – 30 Bq/kg) to that of  $^{232}\text{Th}$  measured by ICP-MS (range 20 Bq/kg – 37 Bq/kg). The fact that the radium and thorium concentrations remain constant with respect to leaching time indicates that these isotopes mainly remain in the heaps.

**Table 11.** Mean activity concentrations (Bq/kg) ( $n = 5$ ) of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$  in the Talvivaara heaps as a function of leaching time, measured by gamma spectrometry. The values are arithmetic means with standard deviation ( $\pm$ ).

Leaching time (y)	$^{214}\text{Pb}/^{214}\text{Bi}(^{226}\text{Ra})$	$^{228}\text{Ac}(^{228}\text{Ra})$	$^{208}\text{Tl}/^{212}\text{Pb}(^{228}\text{Th})$
0	115 $\pm$ 7	26 $\pm$ 1	27 $\pm$ 1
0.5	200 $\pm$ 50	27 $\pm$ 8	30 $\pm$ 10
1	220 $\pm$ 20	27 $\pm$ 6	25 $\pm$ 5
1.5	200 $\pm$ 30	20 $\pm$ 3	19 $\pm$ 5
2	180 $\pm$ 20	17 $\pm$ 2	19 $\pm$ 3
2.5	200 $\pm$ 20	22 $\pm$ 2	21 $\pm$ 2

The ore samples were also analysed for their  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  activity concentrations and uranium and thorium isotopes ( $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{230}\text{Th}$ ,  $^{228}\text{Th}$ ) by alpha spectrometry, after separation by anion exchange chromatography (Table 12). The concentrations for  $^{210}\text{Pb}$ ,  $^{210}\text{Po}$ ,  $^{228}\text{Th}$ ,  $^{230}\text{Th}$  or  $^{232}\text{Th}$  vary randomly from 195 Bq/kg

to 150 Bq/kg for  $^{210}\text{Pb}$ , from 222 Bq/kg to 170 Bq/kg for  $^{210}\text{Po}$ , from 35 Bq/kg to 15 Bq/kg for  $^{228}\text{Th}$ , from 293 Bq/kg to 122 Bq/kg for  $^{230}\text{Th}$ , and from 25 Bq/kg to 14 Bq/kg for  $^{232}\text{Th}$ . In the case of  $^{238}\text{U}$  and  $^{234}\text{U}$ , the activity concentrations decrease in the leached ore during the leaching process from 338 Bq/kg to 89 Bq/kg and from 230 Bq/kg to 86 Bq/kg, respectively. This clearly indicates the mobilization of uranium to the pregnant leach solution.

**Table 12.** Activity concentrations (Bq/kg) of  $^{210}\text{Po}$ ,  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{228}\text{Th}$  in the ore samples collected from the Talvivaara heaps, measured by alpha spectrometry.  $^{210}\text{Pb}$  was determined from the ingrowth of  $^{210}\text{Po}$ .

Leaching time (y)	$^{210}\text{Pb}$ (unc. 6%)	$^{210}\text{Po}$ (unc. 9%)	$^{228}\text{Th}$ (unc. 15%)	$^{230}\text{Th}$ (unc. 15%)	$^{232}\text{Th}$ (unc. 15%)	$^{234}\text{U}$ (unc. 14%)	$^{238}\text{U}$ (unc. 14%)
0	n.d	n.d	35	293	23	230	338
0.5	195	222	25	263	25	216	211
1.0	164	174	15	122	15	101	107
1.5	171	175	22	227	23	115	127
2.0	167	178	17	138	14	110	105
2.5	150	170	20	224	23	86	89

n.d. – not determined

Table 13 presents the isotopic ratios of  $^{210}\text{Po}/^{210}\text{Pb}$ ,  $^{228}\text{Th}/^{232}\text{Th}$ ,  $^{234}\text{U}/^{238}\text{U}$ ,  $^{238}\text{U}/^{210}\text{Po}$  and  $^{234}\text{U}/^{230}\text{Th}$  as a function of leaching time in the samples collected from the Talvivaara heaps. The isotopic ratios of  $^{234}\text{U}/^{238}\text{U}$  are close to unity throughout the leaching process, and therefore no isotopic fractionation has taken place. The  $^{228}\text{Th}/^{232}\text{Th}$  ratio decreases during heap leaching, which indicates slight mobilization of  $^{228}\text{Th}$ . The  $^{210}\text{Po}/^{210}\text{Pb}$  ratio is slightly elevated (1.1 on average), which might indicate slight mobilization of lead. The ratios of  $^{238}\text{U}/^{210}\text{Po}$  and  $^{234}\text{U}/^{230}\text{Th}$  ratios are clearly lowered during the leaching process, which again indicates that uranium has been partly mobilized from the ore to the pregnant leach solution.

**Table 13.** Isotopic ratios of  $^{210}\text{Po}/^{210}\text{Pb}$ ,  $^{228}\text{Th}/^{232}\text{Th}$ ,  $^{234}\text{U}/^{238}\text{U}$ ,  $^{238}\text{U}/^{210}\text{Po}$  and  $^{234}\text{U}/^{230}\text{Th}$  in the samples collected from the Talvivaara heaps (uncertainty app. 10%).

Leaching time (y)	$^{234}\text{U}/^{238}\text{U}$	$^{238}\text{U}/^{210}\text{Po}$	$^{234}\text{U}/^{230}\text{Th}$	$^{228}\text{Th}/^{232}\text{Th}$	$^{210}\text{Po}/^{210}\text{Pb}$
0	0.68	n.d.	0.78	1.52	n.d.
0.5	1.02	0.95	0.82	1.00	1.14
1.0	0.94	0.61	0.82	1.00	1.06
1.5	0.91	0.73	0.51	0.96	1.02
2.0	1.05	0.59	0.80	1.21	1.07
2.5	0.97	0.52	0.38	0.87	1.13

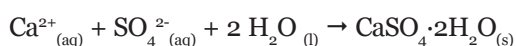
n.d. – not determined

Uranium is mostly hosted by uraninite in the black schist ore of Talvivaara based on EPMA studies. In heap leaching of the crushed ore, uranium is dissolved from uraninite in the pregnant leach solution. This is shown by 1) disappearance of uraninite in the leached ore already after half-year leaching (based on EPMA), 2) significant presence of uranium in the pregnant leach solution (based on ICP-MS), and 3) decrease in uranium concentration of the leached ore in the heaps as a function of leaching time (based on ICP-MS, gamma and alpha spectrometry). However, uranium is not entirely mobilized from the heaps to solution during leaching, which may be related to the precipitation of secondary minerals in the heaps. The main secondary minerals are jarosite, goethite, and gypsum. Based on EPMA studies, goethite in the leaching heaps is uraniferous, possibly resulting from the sorption of U(VI) to goethite. In general, uranium is not significantly incorporated in jarosite (Dutrizac and Chen 2009) and the low U contents detected in jarosite by EPMA could reflect just retained pregnant leach solution in the jarosite precipitates in the heaps.

After leaching of metals, the leaching solution is diverted to ponds that correspond to each heap. Uranium and thorium concentrations in the PLS solutions were measured by ICP-MS. The uranium concentration was the highest, 28 ppm, in the youngest PLS pond, corresponding to the heap that had been leached for 0.5 years. In the other three ponds, the concentrations were the same within analytical uncertainty (range 15 – 19 ppm, uncertainty 2 ppm). This indicates that most of the uranium is leached after half a year. The concentration of thorium in the PLS is low (range 0.2-0.5 ppm) and does not vary significantly with respect to leaching time.

Components of the pregnant leach solution tend to precipitate in contact with oxygen. This was observed in the laboratory when sampling bottles were opened. After a few days, the colour changes from green to reddish brown and precipitation occurs. XRD measurements revealed that this precipitate consists of gypsum and natrojarosite (approximately 50-50%). The precipitate samples were measured by gamma spectrometry to determine activity concentrations of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{228}\text{Th}$ , and  $^{238}\text{U}$ . The activity concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  were mostly below the limit of detection. The activity concentrations of  $^{228}\text{Th}$  were also low, varying from 0.3 Bq/kg to 0.5 Bq/kg. However, uranium concentrations varied from 115 Bq/kg up to 220 Bq/kg in the PLS precipitates.

After metals recovery, resulting slurry is diverted to gypsum ponds. In these ponds, the main minerals are gypsum and calcite, with amounts of 50% and 45%, respectively, based on XRD analysis. Calcite and dolomite are used in pH adjustment during removal of residual metals. Gypsum is precipitated when limestone ( $\text{CaCO}_3$ ) and lime are used for pH adjustment in iron removal and final neutralization, respectively:



Gypsum pond tailings also contain iron hydroxides, which are derived from iron removal and the final neutralization processes (Pitkääjärvi 2009). A single uraniferous goethite grain was found in the gypsum pond precipitate, containing 870 ppm U. No uranium was observed in the gypsum itself, though the detection limit of uranium by EPMA is high (490 ppm U).

The uranium content of the gypsum precipitate is highly variable (6-260 ppm U), being about 100 ppm U on average. The solid samples were also measured by gamma spectrometry to determine activity concentrations of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{228}\text{Th}$  and  $^{238}\text{U}$  in the gypsum ponds (Table 14). The concentrations of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{228}\text{Th}$  are low, which indicates that these nuclides mostly remain in the heaps. The concentration of  $^{238}\text{U}$  varies from 1008 Bq/kg to 3447 Bq/kg, which indicates dissolution of uranium from uraninite to the pregnant leach solution, finally ending up to precipitates of the gypsum pond tailings via removal of non-valuable residual metals, i.e. during iron removal.

**Table 14.** Activity concentrations (Bq/kg) of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{228}\text{Th}$ , and  $^{238}\text{U}$  in the solid samples from the Talvivaara gypsum pond, measured by gamma spectrometry.

Sample code	$^{226}\text{Ra}$	$^{228}\text{Ra}$	$^{228}\text{Th}$	$^{238}\text{U}$
T-1	10	3	11	1325
T-4b	6.7	4.2	21	3447
T-5a	6.8	1.2	6.2	1008

Table 15 presents activity concentrations (Bq/kg) of  $^{210}\text{Po}$ ,  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{228}\text{Th}$  measured by alpha spectrometry in the solid samples collected from the gypsum pond. The concentrations of  $^{210}\text{Pb}$ ,  $^{210}\text{Po}$ ,  $^{228}\text{Th}$  and  $^{232}\text{Th}$  are low, indicating that these nuclides mainly remain in the heaps. In the case of  $^{238}\text{U}$  and  $^{234}\text{U}$ , the concentrations are higher than in the original ore, which is again an indication of the enrichment of uranium in the gypsum pond precipitates.

**Table 15.** Activity concentrations (Bq/kg) of  $^{210}\text{Po}$ ,  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{230}\text{Th}$  and  $^{228}\text{Th}$  in the solid samples collected from the gypsum pond, measured by alpha spectrometry.  $^{210}\text{Pb}$  was determined from the ingrowth of  $^{210}\text{Po}$ .

Sample code	$^{210}\text{Pb}$ (unc. 6%)	$^{210}\text{Po}$ (unc. 9%)	$^{228}\text{Th}$ (unc. 15%)	$^{230}\text{Th}$ (unc. 15%)	$^{232}\text{Th}$ (unc. 15%)	$^{234}\text{U}$ (unc. 14%)	$^{238}\text{U}$ (unc. 14%)
T-1	n.d.	n.d.	7	154	14	1317	1302
T-4a	2	2	0.6	3	0.7	64	58
T-4b	3	13	15	386	40	3425	3375

n.d. - not determined

Table 16 show isotopic ratios of  $^{210}\text{Po}/^{210}\text{Pb}$ ,  $^{228}\text{Th}/^{232}\text{Th}$ ,  $^{234}\text{U}/^{238}\text{U}$ ,  $^{238}\text{U}/^{210}\text{Po}$  and  $^{234}\text{U}/^{230}\text{Th}$  in the solid samples collected from the gypsum pond. The isotopic ratio of  $^{234}\text{U}/^{238}\text{U}$  is again close to unity, which indicates that no isotopic fractionation

has taken place in the production process. The ratios of  $^{238}\text{U}/^{210}\text{Po}$  and  $^{234}\text{U}/^{230}\text{Th}$  ratios are clearly elevated which is a clear indication that  $^{210}\text{Po}$  and  $^{230}\text{Th}$  mainly mostly remain in the heaps.

**Table 16.** Isotopic ratios of  $^{210}\text{Po}/^{210}\text{Pb}$ ,  $^{228}\text{Th}/^{232}\text{Th}$ ,  $^{234}\text{U}/^{238}\text{U}$ ,  $^{238}\text{U}/^{210}\text{Po}$  and  $^{234}\text{U}/^{230}\text{Th}$  in the samples collected from the Talvivaara gypsum pond (uncertainty approximately 7%).

Sample code	$^{234}\text{U}/^{238}\text{U}$	$^{238}\text{U}/^{210}\text{Po}$	$^{234}\text{U}/^{230}\text{Th}$	$^{228}\text{Th}/^{232}\text{Th}$	$^{210}\text{Po}/^{210}\text{Pb}$
T-1	1.01	n.d	8.55	0.50	n.d
T-4a	1.10	29.0	21.3	0.86	1.00
T-4b	1.01	259.6	8.87	0.38	4.33

n.d - not determined



## 5 CONCLUSIONS

A well-planned and tested procedure can lead to reliable results. The first article aimed to obtain analytical verification of field results, so that the site characterization could be optimized without compromising reliability of the analysis. The results showed that overall, a sample mass of 0.1-0.5 g with addition of 20 mL concentrated nitric acid is the most efficient means of extracting uranium and thorium simultaneously from apatite ore, black schist and mill tailings. The results for uranium and thorium concentrations determined by gamma spectrometry, alpha spectrometry, and ICP-MS were in good agreement. Also the on-site measurements with portable XRF gave comparable results to other methods used in this study for thorium, even without prior sample preparation.

The mobilization of radionuclides and heavy metals from the mill tailings at Sokli was examined in order to assess the potential environmental impact of past and future mining activities. There was no indication from mineralogical studies that uranium or thorium has been mobilized from altered pyrochlore-group minerals in the Sokli ore or tailings. From the considerable amount of apatite still present in the latter, the material does not represent actual tailings, or at least, pilot milling tests failed because apatite, the target ore mineral, was not extracted successfully from the ore. When studying the vertical and horizontal mobilization in the tailings pond, there is no clear trend either in the activity concentrations of uranium, radium and thorium isotopes in the surface layers of the mill tailings. In subsurface samples, an increase in these isotopes can be seen when approaching the pond at the distal end of the sludge field. Since there is no obvious reason for lateral subsurface migration without at least some vertical mixing and, because of the positive correlation of these nuclides in subsurface samples, the increase in concentrations is most likely to have been caused by compositional changes in material discharges. Sequential extraction results suggest that uranium (4%) is partly soluble under weakly acidic conditions, whereas thorium is tightly bound. In conclusion, at present the Sokli mining site has had only a limited impact on the surrounding area, because mill tailings were derived from physical removal of gangue at an early stage of the mining process and phosphoric acid was not produced on site. However, this may change if aggressive chemical treatments would be applied.

At the former Paukkajanvaara uranium mine in Eno, the aim of the study was to examine the potential for further mobilization of radionuclides after remediation. Based on the results, there seems to be leaching of at least  $^{226}\text{Ra}$  from the waste rock pile and/or tailings repository.  $^{226}\text{Ra}$  has been leached from the waste rock pile to surrounding soil and further to the run-off sediment. Also uranium is enriched in this sediment. During spring floods, these nuclides emanate further in the stream.

Increases of uranium concentrations could be detected after the stream had passed the tailings area. There is also evidence for vertical leaching of  $^{226}\text{Ra}$  in the tailings repository and the analytical results from the soil samples collected between the repository and the stream suggest that this might be the possible contamination pathway. Finally, the leakage of  $^{226}\text{Ra}$  can be seen in the top layers of the Lake Iso Hiislampi sediments.

At Talvivaara, the aim of the study was to generate new data leading to a better understanding of the fate of radiotoxic daughter nuclides of uranium, primarily  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ , in the mining process. During the heap leaching process, uranium is dissolved from uraninite to the pregnant leach solution. Uranium is probably transported as uranyl ions and uranyl sulfate complexes in the acid pregnant leach solution, and is finally ended up in precipitates of the gypsum pond tailings after the iron removal and the final neutralization processes during the removal of residual metals. In terms of the radiation safety, the  $^{238}\text{U}$  activity concentrations in the gypsum pond are partly above the exemption value (1000 Bq/kg) for natural radionuclides of the  $^{238}\text{U}$  series. Radium and thorium mostly stay in the heaps during heap leaching. In addition,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  stay mainly in the heaps but slight mobilization of these nuclides was indicated. Secondary sulfate minerals, such as gypsum and jarosite, are precipitated from the sulfate-rich and acid PLS at Talvivaara. These minerals can incorporate radium in their crystal lattices, limiting the  $^{226}\text{Ra}$  mobility. Therefore, it can be assumed that most of radium and possibly part of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  are co-precipitated with poorly soluble sulfates in the Talvivaara heaps.

The mobilization of radionuclides is highly dependent on the type of ore (mineralogy, depositional environment, host rock, etc.) and the milling process. Since all three study sites of this thesis represent three totally different ore types and milling processes, the comparison is difficult. However, in the future, problems may arise from acid mine drainage (AMD) development at the Talvivaara and Paukkajanvaara sites. The ores at both sites contain sulfides, which might lead, over time, to AMD and subsequent mobilization of the remaining radionuclides, causing severe environmental problems. Therefore, the knowledge of the behaviour of radionuclides at mining sites is crucial in order to select appropriate remediation techniques and avoid potential environmental legacy problems in the future.

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