

# Levels of natural radionuclides in water and sediments from mining lakes in sweden

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## 1. Introduction

The effect of mining activities in a country as Sweden (the major metal mining country in the European Union) implies enormous quantities of generated mining wastes. Historically, more than 2700 mines gather around 30000 sites that have been minor mines and quarries (according to the database of Geological Survey of Sweden, SGU [Norlin, 2016]). In 1950, there were around 100 active mines while nowadays no more than 15 active mines still remains with ongoing extractions. Many of these sites had opencast mines. During exploitation by open-pit mining, the water table is suppressed to avoid the flooding of active mines. However, when mining activity ceases, the water table recovers its original position, flooding the open pits and giving rise to mine pit lakes.

The environmental problem arises because these waters can be affected by Acidic Mine Drainage (AMD), having high/very high concentration of heavy metals in solution. Apart from the impact to the ecosystem, many of these places are nearby populated areas and most of these water bodies are usually used for recreational purposes (swimming, fishing, diving...) by inhabitants of these former mining areas.

Many works have been conducted to investigate the limnological and geochemical features of a pit lake [Castro, 1998; Stevens and Laurence, 1998; Shevenell, 2000; Ming Lu, 2004] measuring several parameters in waters (pH, temperature, conductivity, dissolved oxygen (DO) or redox potential among others), and the metal concentration. Another group of works with pit lakes are devoted to the study of the remediation of its acid/contaminated waters [Fischer and Guderitz, 1996; Lewis et al., 2003] where the neutralization of lakes is obtained by addition of bases, such as lime, caustic soda or alkaline material. However, really little bibliography can be found about pit lakes all over the world focusing their attention on naturally occurring radionuclides, coming mainly from <sup>238</sup>U and <sup>232</sup>Th series.

Based on previous experiences in Spanish pit lakes [Manjón et al., 2013; Manjón et al., 2014], it was shown that an enhancement on levels in natural radionuclides can occur at these sites. As an example, a non affected water should have around 15 to 30 mBq/L of <sup>238</sup>U while in these sites there was <sup>238</sup>U ranging from 14 to 1110 mBq/L what implies up to 50 times higher than environmental level. This was directly related to the AMD processes at these sites.

This work will try to add more data to this framework, through the measurement of levels of activity concentration in waters and sediments from these special water bodies.

## 2. Materials and Methods

### *Samples*

There were two sampling campaigns (Figure 1. Left). During the 1<sup>st</sup> sampling (March 2015), a set of 23 sites in Central and Southern Sweden (mainly old mines/quarrels from 18<sup>th</sup> and 19<sup>th</sup> century) were sampled. A total of 25 superficial waters and 23 sediment/rocks were sampled in this stage. A second sampling (July 2015) in Northern Sweden (with bigger pit lakes in mining areas from the 20<sup>th</sup> century with less interaction of humans) a total of 20 sites provided 46 superficial waters and 34 sediment/rocks.

The radiometric characterization was carried out via Alpha spectrometry (to be applied in water and sediment) and Gamma spectrometry (to be applied in sediments).

### *Radiometric technique: alpha spectrometry*

In order to apply this technique, samples need to be pretreated to isolate the element of interest and finally, alpha sources are produced in steel disks for U/Th and copper for Po measurements. U isotopes will be <sup>238</sup>U, <sup>235</sup>U and <sup>234</sup>U. Th ones are <sup>232</sup>Th and <sup>230</sup>Th while <sup>210</sup>Po is the only measured isotope of Po.

Depending on the matrix, samples will require different process:

Water samples (~ 0.5 L) were firstly acidified at pH ~2 and spiked with a known amount of tracers (<sup>232</sup>U, <sup>229</sup>Th and <sup>209</sup>Po). Pre-concentration of radionuclides in water samples was carried out through the iron hydroxide precipitation. Then the isolation process was performed using UTEVA resins and finally U, Th fractions were electroplated separately in steel disks while Po fraction followed an instant deposition process using silver disk. For more details about this treatment check [Lehritani et al, 2012].

Sediment/rock samples (~ 1 g) were digested using a microwave (Multiwave 3000), from Anton Paars, equipped with a rotor (eight closed vessels) which allows us to work under controlled pressure until 260°C without the losses of any volatile element during the digestion process. Once the samples were digested, solutions follow an iron hydroxide precipitation process. Separation process was performed via TBP and finally alpha sources prepared in the same way than for water samples.

Measurement were performed with a Canberra Alpha-Analyst system using Passivated Implanted Planar Silicon (PIPS) detectors with independent counting chambers for U, Th and Po. In 240000s measurements, this system provide a MDA (Minimum Detectable Activity) of 0.5 mBq for most of the isotopes.

### *Radiometric technique: gamma spectrometry*

The radionuclides to be measured by  $\gamma$ -spectrometry are, belonging to <sup>238</sup>U series: <sup>210</sup>Pb (45.6 keV), <sup>234</sup>Th (63.3 keV), <sup>226</sup>Ra will be determined by secular equilibrium using the  $\gamma$ -ray emissions of <sup>214</sup>Pb (351.9 and 295.2 keV) and <sup>214</sup>Bi (609.3, 1120.3, 1238.1 and 1764.5 keV). Also <sup>234</sup>Pa (1001.0 keV) will be measured when possible (due to its very low gamma yield). Regarding <sup>232</sup>Th series: <sup>228</sup>Ra can be obtained via <sup>228</sup>Ac (338.3, 911.2 and 968.9 keV). <sup>228</sup>Th activity concentrations will be determined through emissions of <sup>212</sup>Pb (238.6 keV), <sup>212</sup>Bi (727.3 keV) and <sup>208</sup>Tl (583.2, 860.6 and 2614.5 keV). Isotopes from <sup>235</sup>U series, with an activity concentration around 20 times lower than

isotopes from the  $^{238}\text{U}$  one, will be seldom detected, but in such a cases, the  $\gamma$ -lines used for its measurements are:  $^{227}\text{Th}$ (50.1 and 235.9 keV),  $^{235}\text{U}$  (163.4, 205.3 keV). Also, the  $^{40}\text{K}$  activity concentration was determined directly from its emission line at 1460.8 keV and the anthropogenic  $^{137}\text{Cs}$  from 661.67 keV.

In case of Sediment/rocks, samples were dried, grinded and then packaged in Petri disk. Samples were sealed and stored for 3/4 weeks before being measured in order to reach secular equilibrium between  $^{226}\text{Ra}$  and its daughter. Measurements were carried out with an extended range Germanium coaxial detector (XtRa) of 37.1% relative efficiency and 1.76 keV resolution. This system has a 10 centimetres passive shielding of ancient lead and an active shielding made with an organic scintillation detector (Bicron BC-418) that works in anti-coincident mode with the Ge detector resulting in very low background level [Hurtado et al., 2007]. In 200000s measurements, this system provide a MDA of 0.55Bq for  $^{210}\text{Pb}$  (45.6 keV), 0.38 Bq for  $^{214}\text{Pb}$  (351.9 keV), 0.30 Bq for  $^{214}\text{Bi}$  (609.3 keV) or 1.62 Bq for  $^{40}\text{K}$  (1460.8 keV) among others radionuclides of interest.

### *In situ measurements*

Once at the different sites, an external dose measurement was performed at every place with two independent detectors that were placed 1 m above the ground during the sampling time. The final result was an average over 15 to 20 minutes for each site. The equipment was a Rados SRV 2000 Compensated GM-tube with an energy range: 50 keV - 3 MeV and a dose rate range: 0.05  $\mu\text{Sv/h}$  - 10 Sv/h.

Also a physicochemical characterization was carried out immediately after superficial water was collected. Measurement of temperature (T), pH, Dissolved Oxygen (DO), Oxidation-Reduction Potential (ORP), Specific Conductivity (spC), Total Dissolved Solids (TDS) and Salinity where performed just after superficial water collection using a Hydrolab M5 multiparametric probe.

## **Results and Discussion**

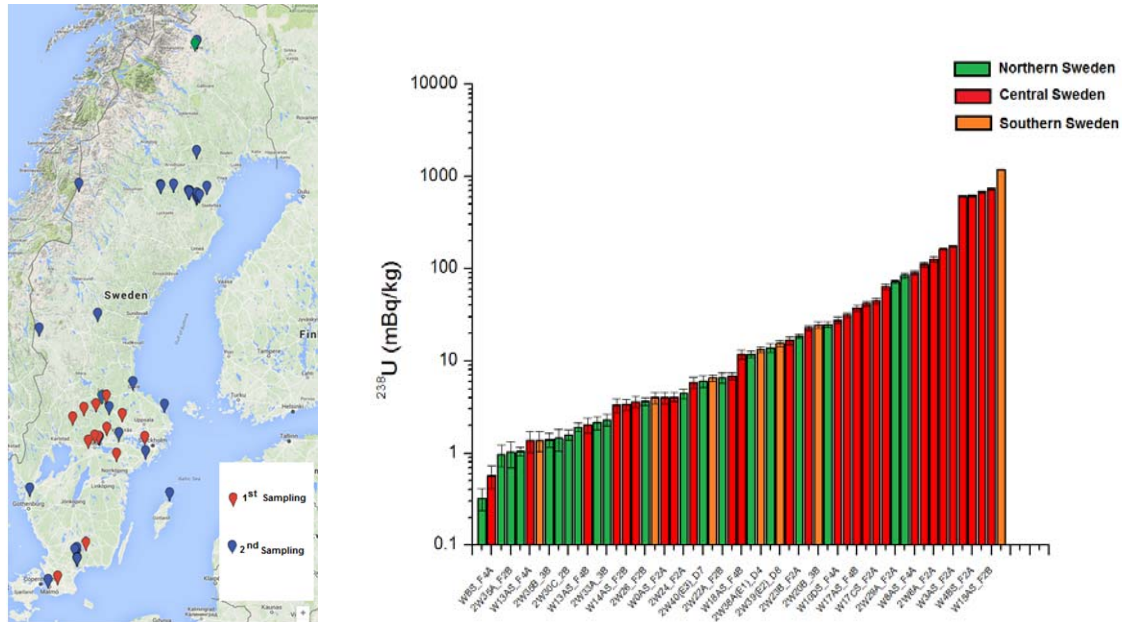
The environmental external gamma dose measurements average  $0.11\pm 0.06\mu\text{Sv/h}$  ranging from 0.05 to 0.37  $\mu\text{Sv/h}$ . The external exposure rates from terrestrial gamma radiation in Sweden according to [Unsear 2000] is 0.056  $\mu\text{Sv/h}$  with a range 0.04 to 0.50  $\mu\text{Sv/h}$ . In this sense, our measurements are within the expected values, however, several sites were identified for having external dose values three times above the average.

### *Results in waters*

Regarding pH in superficial waters, values ranging from 4.4 to 9.33 with an average of  $7.46\pm 0.94$  (one sigma criteria for standard deviation) were found, what implies neutral waters and not many problems due to ADM. It is worth to mention here that, due to several remediation projects in acid/contaminated waters [Boliden, 2015], the neutralization of lakes is obtained by addition of bases, such as lime, caustic soda or alkaline material. This has changed the chemistry of many of these water bodies, especially in the Northern areas.

In pit lakes in Spain [Manjón et al., 2013; Manjón et al., 2014], pH was in the range 2 to 3.5 (extremely acidic waters) finding up to 1110 mBq/kg of  $^{238}\text{U}$ . In Morocco [Mantero et al, 2015] it was found a pH range from 8 to 9.5 (alkaline waters) in former mining lakes, with values of  $^{238}\text{U}$  up to 1037mBq/kg. Alkaline pH values and elevated bicarbonate concentrations favour the stabilization

and mobilization of uranium as uranyl-carbonate complex, [Abdelouas et al.1998]. In contrast, the predominant species in acid, oxygenated waters are the uranyl ion and uranyl-sulfate complex [Wanty et al. 1999]. Attending to Figure 1.Right, it has been found moderate levels of  $^{238}\text{U}$  up to 1183 mBq/kg (pH 5.9) in Sweden what implies different uranium chemistry more associated to bicarbonate complexes.



**Figure 1.** (Left) Sampling map. (Right)  $^{238}\text{U}$  activity concentration in superficial waters from pit lakes in Sweden.

The 74% of the studied pit lakes have environmental levels regarding U isotopes, however 26% are above 50mBq/kg having some enhancement in U elements. It is observed a clear  $^{234}\text{U}/^{238}\text{U}$  ratio higher than one, typical of water bodies interacting with underground waters.

Table 1 summarizes the values obtained by alpha spectrometry in these waters finding out environmental levels for Th and Po isotopes in all cases. It is well-known the tendency of U for being in mobile phases while Th and Po remains into the original matrices fixed to the bedrock. This behaviour is reflected in these data.

Radionuclide	Average (mBq/kg)	Range (mBq/kg)
$^{238}\text{U}$	94	0.3-1183
$^{234}\text{U}$	125	0.3-1700
$^{230}\text{Th}$	3.1	MDA-26
$^{210}\text{Po}$	5.9	1.1 -22

**Table 1.** Summary of results in superficial waters for radionuclides belonging to  $^{238}\text{U}$  series.

Regarding  $^{232}\text{Th}$  activity concentration in superficial waters, results were even lower that the ones of  $^{230}\text{Th}$ . The MDA for this nuclide is 0.5 mBq/kg being 46% of the samples below this threshold.  $^{232}\text{Th}$  ranges from MDA to  $8.8 \pm 2.7$  mBq/kg.

## Results in sediments and rocks

Secular equilibrium in natural series was measured (via gamma spectrometry) in 93% of sediments and 100% of the rocks. In case of  $^{238}\text{U}$  series:  $^{234}\text{Th}$ ,  $^{234}\text{Pa}$ ,  $^{214}\text{Bi}$ ,  $^{214}\text{Pb}$  and  $^{210}\text{Pb}$  had the same activity concentration. The same results among  $^{228}\text{Ac}$ ,  $^{212}\text{Pb}$ ,  $^{212}\text{Bi}$  and  $^{208}\text{Tl}$  from  $^{232}\text{Th}$  series and also secular equilibrium between  $^{235}\text{U}$  and  $^{227}\text{Th}$ . These results have been summarized in Table 2 where also  $^{137}\text{Cs}$  and  $^{40}\text{K}$  are added.

According to [Unsear 2000] the natural radionuclide content (Bq/kg) in soils in Sweden is:  $^{226}\text{Ra}$  from 12-170,  $^{232}\text{Th}$  from 14-94 and  $^{40}\text{K}$  from 560-1150. All these ranges include most of the results for sediments of Table 2 except for one site with higher U and Th values. At this site, there was collected a rock having  $467\pm 35$  Bq/g for  $^{238}\text{U}$  series,  $22\pm 3$  Bq/g for  $^{232}\text{Th}$  series,  $16\pm 3$  Bq/g for  $^{235}\text{U}$  series and  $1.43\pm 0.2$  Bq/g for  $^{40}\text{K}$ .

(Bq/kg)	SEDIMENTS (n=12)		ROCKS (n=13)	
	Average	Range	Average	Range
$^{238}\text{U}$ serie	277	10-1518	54*	3-467000
$^{232}\text{Th}$ serie	63	7-173	52*	4-22000
$^{235}\text{U}$ -serie		MDA-79		MDA-16000
$^{137}\text{Cs}$		MDA-6		MDA
$^{40}\text{K}$	710	56-1405	826	2-2443

**Table 2.** Activity concentration (Bq/kg) in sediments for natural radionuclides (and  $^{137}\text{Cs}$ ) via gamma (n represents the number of analyzed samples).

(\*)For these averages, the rock with 467Bq/g for  $^{238}\text{U}$  and 22Bq/g for  $^{232}\text{Th}$  was not included.

Several sites have been identified for having moderate levels of natural radionuclides and one of them require a more detailed study due to very high activity concentration values and because it's a well known place where local inhabitants.

## Conclusions

A study on the levels of natural radionuclides in pit lakes in Sweden has been carried out in places where local inhabitants interact with former mining lakes. Regarding water samples, Th and Po isotopes were found at environmental levels in these water bodies while several sites in central Sweden were found with enhanced levels of U isotopes. These sites require further investigations mainly focused in U isotopes in order to carry out dose assessments. Concerning sediments/rocks, most of the results are included within the range of typical values in Sweden except for several sites. In one particular place (frequently used by local people for recreational purposes) very high levels were found of natural radionuclides.

## Acknowledgement

This work has been fully funded by SSM (the Swedish Radiation Safety Authority).

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