

^{226}Ra , ^{210}Po and lead isotopes in a pit lake water profile in Sweden

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ABSTRACT

A pit lake arises as a consequence of anthropogenic activities in opencast mining areas. These water bodies may be enriched in hazardous stable contaminants and/or in naturally occurring radionuclides depending on the local geological conditions. Mining legacy in Sweden produced hundreds of these pit lakes and most of them are used for recreational purposes in the southern part of the country. In this paper, one pit lake was selected for having enhanced levels of natural radionuclides. Physico-chemical parameters (temperature, pH, oxidation-reduction potential, dissolved oxygen and depth), elemental composition (via Inductive Coupled Plasma Mass Spectrometry) and radiometric characterization (via alpha spectrometry of ^{226}Ra , ^{210}Po and ^{210}Pb) were carried along the depth of a 60 m depth pit lake, with the main aim to describe how natural radionuclides and elements behaves with depth in a non-uraniferous pit lake.

Based on observed changes in physico-chemical parameters, a thermocline and a chemocline region were identified at around 10 and 30 m depth respectively. Concerning radionuclides, ^{226}Ra ranged from 75 ± 3 up to 360 ± 12 mBq/kg while ^{210}Po ranged from 11 ± 1 up to 71 ± 3 mBq/kg. ^{210}Pb distribution with depth was also determined via secular equilibrium with ^{210}Po after 2 years and also stable Pb was measured. Disequilibrium ^{226}Ra - ^{210}Pb was found and the residence time of ^{210}Pb in the water column was assessed. Additionally, different vertical distributions between ^{210}Pb and Pb were found which points out different sources for different lead isotopes in the water body.

1. Introduction

Pit lakes are anthropogenic water bodies widely studied from the geochemistry perspective as legacy of opencast mining. Thousands of pit lakes all over the world are potentially toxic and pose risks to the environment (Blanchette and Lund, 2016). The study of radionuclides in these sites are less common, except for the case of former U mining sites: in Kazakhstan (Salbu et al., 2013), Tajikistan (Skipperud et al., 2013a) or Brazil (Ferrari et al., 2015) among others. In these sites, ^{238}U in pit lakes was found ranging from 12 to 40 Bq/L. However, non-uraniferous mine pit lakes can be found also with similar ^{238}U levels as in Gammons et al. (2003) where a Cu mine pit lake was found with 10.5 Bq/L. Additionally, enriched ^{238}U levels were found in acidic pit lakes (Manjon

et al., 2015) with 1.1 Bq/L or in alkaline pit lakes with 2.0 Bq/L of ^{238}U (Manjon et al., 2018). As reference, the mean $\pm$ standard deviation for U geochemical background in European continental surface water is 0.011 ± 0.021 Bq/L (De Vos and Tarvainen, 2006).

During 2015, several samplings were conducted throughout Sweden to survey surficial water from former mining sites with water filled pits (Mantero et al., 2020). From among all surveyed sites, one site was found with enhanced levels of ^{238}U (150 mBq/kg), in comparison with typical environmental levels (in the range 10–20 mBq/kg, De Vos and Tarvainen, 2006). In April 2016, a more detailed sampling was performed in this pit lake which results are presented in this work. The mining site in this study was an open-pit feldspar mine, in operation between 1890 and 1980. Due to the geographical location and

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maximum depth, the pit lake is expected to develop stratification layers in winter (ice covered) and summer, while turnover periods could occur in spring and autumn.

Taking in consideration the different behavior of the progeny in the uranium series, this work tackles the following questions: what are the levels of radionuclides from ^{238}U series in a pit lake with enhanced levels of U? Is there any stratification layers, if so, what concentrations of stable elements and radionuclides can be expected at various depths? In addition, how do these concentrations relate to water quality parameters: pH, ORP, SC and DO? To that aim, ^{226}Ra , ^{210}Po and ^{210}Pb were measured in surficial water and along the depth. The elemental perspective added to this work (elemental determinations were performed together with physico-chemical parameters) will contribute to a better understanding of the chemical behavior of the natural radionuclides with depth in this pit lake through the findings of correlations among all the parameters.

In literature, the behavior of natural radionuclides (^{210}Pb and ^{210}Po) in water profiles from aqueous systems (marine environments, rivers or natural lakes) has been widely studied (Thomson and Turekian, 1976; Moore and Smith, 1986; Balistreri et al., 1995; Hong et al., 1999; Mudbidre et al., 2014; Rigaud et al., 2015) but covering wider perspectives and with quite different aims. However, to the best of our knowledge, this paper is the first study regarding a water profile focused in analyzing the behavior of natural radionuclides from non-uraniferous mine pit lakes.

2. Material and methods

2.1. Sampling

The former feldspar mine (Kolsva Fältspatgruva, Fig. 1) is located in Västmanland county in Sweden on a granitic bedrock according to the Geological survey of Sweden (SGU, Geokartan). The association of enhanced levels of radionuclides with granitic substrates has been previously reported (e.g. Reyss et al., 2016). Fig. 1 shows the location of the water body at 59.570445 N, 15.821115 E (WGS 84 coordinates). The pit lake has a perimeter of 430 m and covered surface of 1.06 ha.

Water samples were stored in 5 L plastic containers and immediately acidified to pH 2 with 5 mL of 65% HNO_3 . This fraction was collected for radionuclide analysis and was not filtered in order to enable an

assessment of the total concentration of radionuclides. A second fraction of 45 mL was collected for the ICP-MS measurement and was acidified with ultra-pure 65% HNO_3 . This sample was filtrated in the lab with a qualitative filter paper (35–40 μm pore size) for particle retention (WHATMAN, England). The main aim was to measure the total elementary content in water.

Blanks samples were prepared by adding 65% HNO_3 to distilled water (Milli-Q) and were analysed with the same procedure as for the stable elements (ICP-MS) and radionuclides (alpha spectrometry). Independently, during the ICP-MS measurements, blank samples were included in every batch as an internal quality control of the laboratory.

2.2. In situ measurements

2.2.1. Echo sounder

The bathymetry and the deepest depth of the pit lake was measured and located with a Helix 5SI echo sounder (Fig. 2) together with the software Autochart Pro (Humminbird), which provided 2D and 3D images of the lake bottom (Fig. S1, from Supplementary material).

2.2.2. Physico-chemical parameters

Measurement of temperature (T), pH, Dissolved Oxygen (DO), Oxidation-Reduction Potential (ORP), Specific Conductivity (SC) and depth (m) were performed in situ over the deepest spot of the pit lake, using a Hydrolab MS5 (Fig. 2) multiparametric water probe. This instrument was calibrated with certified standards solutions for pH, SC and ORP at the beginning of each sampling campaign.

2.3. Elementary and radiometric characterization

2.3.1. ICP-MS/MS

ICP-MS measurements were performed at the CITIUS laboratory at the University of Seville with a tandem mass spectrometer (ICP MS/MS), model Agilent 7500c. This technique measures the elementary composition of water samples with major (Na, Mg, Al, K, Ca) and trace elements (Fe, Mn, Cr, Zn, Sr, Ba, V, Rb, Y, La, Ce, W, Pb, Th and U). A Multi-element calibration standard solution containing: Al, Sb, As, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, Th, U, V and Zn was used in every analysis sequence which also included blank samples to control the performance throughout the measurement sequence. The detection limit is below 0.1



Fig. 1. Location Map, from Google Earth and picture of the Kolsva Fältspatgruva site (Photo by Juan Mantero, April 2016).



Fig. 2. Different probes and sampling systems used during this project. From left to right: the fully-equipped boat, Hydrolab M5 multiparametric water probe, Helix 551 echo sounder and Niskin bottle.

$\mu\text{g/kg}$ (ppb) for most of the trace elements in this system. For U and Th, the concentration in $\mu\text{g/kg}$ are calculated to mBq/kg by using 12.45 and 4.06 conversion factors respectively. The relative uncertainty (95% confidence level) for these elements ranged between 10 and 20%. This system was cross-checked in [Mantero et al. \(2019\)](#), being found good performance in the quality of the produced data.

2.3.2. Radiochemical procedure for radium and polonium

In order to apply the alpha-particle spectrometric technique, water samples need to be pretreated to isolate the element of interest and finally, alpha sources are produced in steel disks for Ra while copper disks were produced for Po measurements.

Regarding radium analysis, water samples were spiked with ^{229}Th tracer ($177.6 \pm 1.1 \text{ mBq}\cdot\text{g}^{-1}$) in equilibrium with progeny ^{225}Ra . The Ra isolation from interfering natural radionuclides is based on ion-chromatographic resins: AG1X8 and AG50X8. The first resin (AG1X8) removes Th from the sample, and the second one (AG50X8) isolates Ra from Ac isotopes and other interfering natural radionuclides. The whole process is described in [Pérez-Moreno et al. \(2019\)](#).

Concerning polonium, water samples ($\sim 0.5 \text{ L}$) are firstly acidified to $\text{pH} \sim 2$ and spiked with a known amount of ^{209}Po tracer. Pre-concentration was carried out by iron hydroxide precipitation and then the Po was isolated from actinides by liquid-liquid extraction using TBP and was finally by inducing a self-deposition process using copper disks ([Díaz-Frances et al., 2013](#)).

Activity concentrations of ^{210}Pb were determined through ingrowth of ^{210}Po by alpha spectrometry, analyzing a second 0.5 L aliquot from the same 5 L bottle two years after sampling, when secular equilibrium with ^{210}Po can be assumed.

Prepared alpha sources (both for Ra and Po) were measured in an Alpha Ensemble system (Ortec) equipped with 8 ULTRA Ion-Implanted-Silicon Charged-Particle detectors housed each one inside a vacuum chamber. Due to the low activity concentration levels in water samples, typical times of $200\text{--}10^3 \text{ s}$ were used to obtain relative uncertainties in activity concentration around 5%. In general, a Minimum Detectable Activity (MDA) below 1 mBq for ^{226}Ra and ^{210}Po isotopes were reached.

2.4. Statistical analysis

A Principal Component Analysis (PCA) has been applied to chemical data looking for relationships between variables using XLSTAT software (www.xlstat.com). The application of PCA permits reducing the number of variables in a multivariate data without losing much variation present in the data set. Variables were also standardized to z-scores to fit a normal distribution and thus, the Pearson (n-1) correlation matrix was used ([Davis, 2002](#)).

3. Results and discussion

All uncertainties shown in Tables and error bars from Figures in this work follow the 1-sigma criteria.

3.1. Bathymetry and physico-chemical parameters

Initially a bathymetric map ([Fig. 1S](#)) was generated to identify the deepest place of the lake, then the physico-chemical parameters were measured along the depth. Changes in the physico-chemical profile were used to select the water sampling depths. Attending to those variations in the vertical profile ([Fig. 3](#) water samples (using a 5 L Niskin bottle, [Fig. 2](#)), were collected at: 0, 10, 20, 25, 30, 35, 40, and 50 m depth.

According to pH and SC values and following [Eary \(1999\)](#) categorization, this lake can be classified as circumneutral-Low TDS pit lake, characterized for having minimally reactive wall-rocks surfaces on the pit. A sharp gradient in temperature (T) ([Fig. 3](#)) set a thermocline around 10 m depth. An oxic layer was found from the surface down to 30 m depth. In the range $30\text{--}40 \text{ m}$ depth (suboxic layer), changes in pH, ORP or DO confirm the existence of a chemocline with anoxic ($\text{DO } 0\text{--}0.5 \text{ mg/L}$) and reduced (ORP around 100 mV) conditions from 40 m until the bottom. SC values around $100 \mu\text{S/cm}$ shows poor mineralization in the water column for the range $0\text{--}30 \text{ m}$ while additional mineralization occurs from the chemocline downwards. (Raw data to generate [Fig. 3](#) are presented as [Table S1](#) in Supplementary material).

3.2. Radiometric characterization

3.2.1. Quality control

As mentioned before, blank samples were prepared on a regular basis for reagents and background control in every batch of samples. In case of Po blank samples measurements, ^{209}Po Region of Interest (ROI) in the alpha spectrum is affected by some counts (in the range $0.2\text{--}0.10$ counts per day, cpd.) while ^{210}Po ROI is in the range $0.04\text{--}0.08$ cpd. depending on the detector used. For Ra blank samples, count rates in the ^{217}At (ingrowth from tracer ^{229}Th) ROI ranges from 0.20 to 0.52 cpd while ^{226}Ra ROI was higher (in the range $1\text{--}5$ cpd) being mostly affected by the background of the detector (recoil effect). The contribution of the chemical reagents was not detected by performing measurements with and without the blank disks in the alpha chambers for both radionuclides.

As part of the quality control applied in this project a surficial water sample was collected in each lake surveyed and two aliquots of each water sample (16 samples) were measured in two different laboratories: Lab 1 a newly setup laboratory and Lab 2, a 30-years experienced laboratory in environmental radioactivity measurements. [Fig. 4](#) shows the Po results of this intercomparison exercise with good agreement. The black circle in the figure shows the activity concentration of ^{210}Po in surficial water for the pit lake included in this work, at the time of the

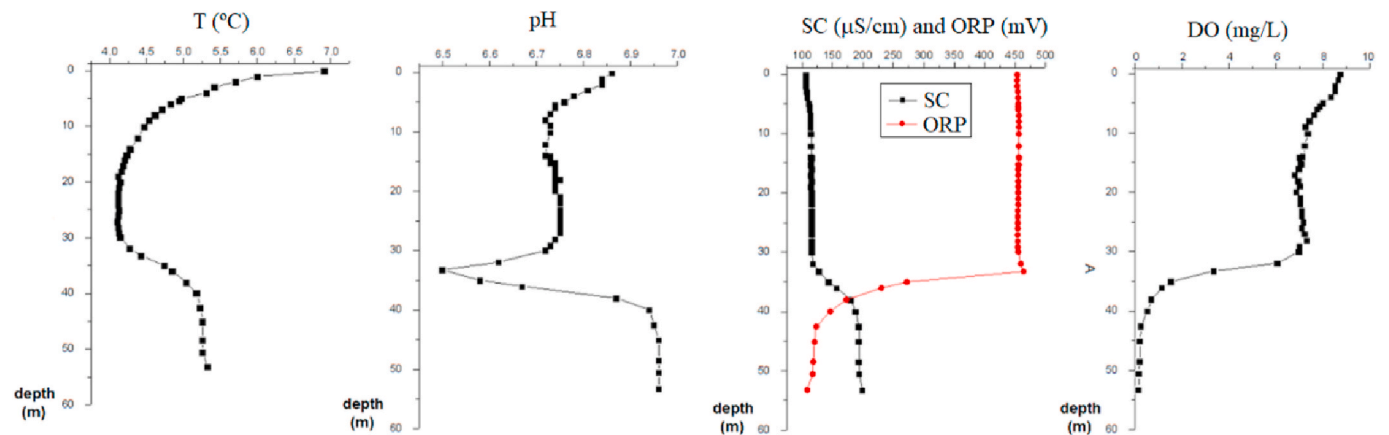


Fig. 3. Vertical distribution of T, pH, ORP, SC and DO.

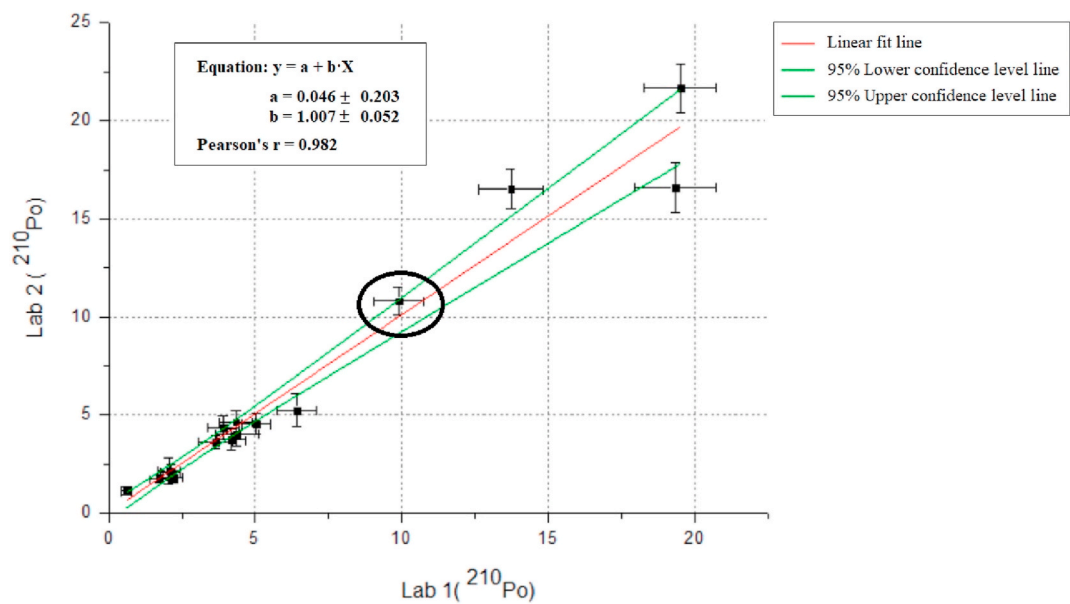


Fig. 4. Intercomparison between two laboratories for ^{210}Po results (in mBq/kg) in 16 surface water samples, from a survey of pit lakes in Southern Sweden in 2015. The black circle marks the result of a surficial water sample from the same pit lake studied in this work, and collected in a previous sampling in 2015.

survey in 2015 (Lab 1: 9.9 ± 0.9 mBq/kg, Lab 2: 10.8 ± 0.7 mBq/kg). These ^{210}Po values are similar to those measured in this work in spring 2016 (11.0 ± 1.2 mBq/kg), indicating non-measurable changes in surface water concentration during the two years.

Quality control of the Ra measurements includes blank samples, and several replicates of a water sample from the 2010 NPL proficiency test exercise (PTE). This water sample was labelled as AL (low level mixture of alpha emitters) during the exercise (Harms and Gilligan, 2011). The obtained result in the NPL test and the obtained by us in this exercise are shown in Table 1, being evident that a good agreement was achieved. High recovery yields were obtained in all the replicated analysis.

Similarly, the average chemical yield $\pm$ SD for the 8 samples of the analysed profile were $76 \pm 13\%$ for ^{226}Ra , and $69 \pm 5\%$ for ^{210}Po . The relative low deviation confirms a robust methodology for Ra and Po analysis in water samples.

3.2.2. Activity concentration

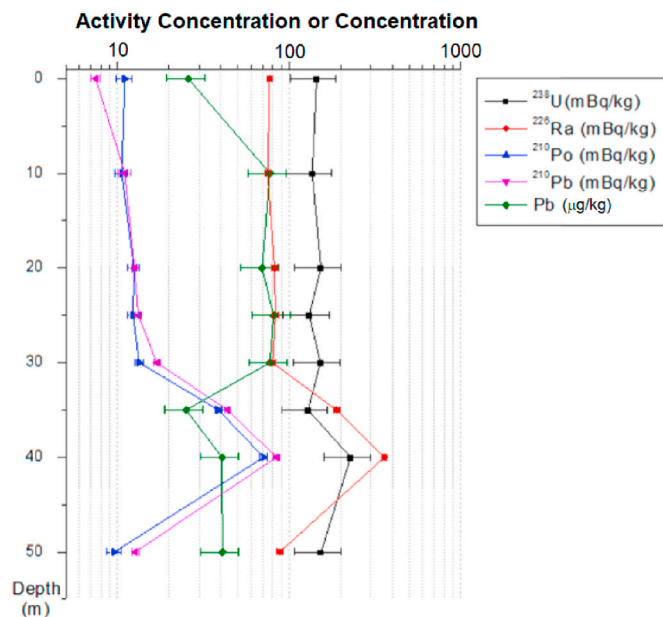
As is shown in Table 2 and Fig. 5, activity concentrations of the radionuclides are not constant with depth, the ratio between maximum and minimum values are 2, 5, 11, 7 and 3 times for ^{238}U , ^{226}Ra , ^{210}Pb , ^{210}Po and Pb respectively. Activity concentration of ^{232}Th was found below or around the detection limit and was mainly detected in the suboxic layer,

Table 1
Results obtained in the analysis of 3 replicates of ^{226}Ra certified reference material from NPL.

	Measured activity values (Bq/kg)	Ra chemical Yield (%)	Z-score
NPL-1	11.2 ± 0.6	73	$Z = \frac{\text{Value}_{\text{Ref}} - \text{Average}_{\text{Measured}}}{\text{St. Dev.}}$
NPL-2	10.4 ± 0.5	78	
NPL-3	10.1 ± 0.5	79	
Average $\pm$ St. Dev.	10.6 ± 0.6	77 ± 3	
NPL Reference Value: 10.8 ± 0.6			0.3

Table 2Activity concentration in ^{238}U series and ^{232}Th radionuclides, and elemental Pb concentration in the vertical water profile. ^{238}U , ^{232}Th and Pb were measured by ICP-MS.

Depth(m)	^{238}U (mBq/kg)	^{226}Ra (mBq/kg)	^{210}Pb (mBq/kg)	^{210}Po (mBq/kg)	Pb($\mu\text{g/kg}$)	^{232}Th (mBq/kg)
0	144 $\pm$ 29	77 $\pm$ 3	7.9 $\pm$ 0.5	11.0 $\pm$ 1.2	26 $\pm$ 5	<0.10
10	136 $\pm$ 27	75 $\pm$ 3	11.0 $\pm$ 0.9	10.6 $\pm$ 0.9	77 $\pm$ 15	0.2 $\pm$ 0.1
20	153 $\pm$ 31	82 $\pm$ 3	12.5 $\pm$ 0.5	12.4 $\pm$ 1.0	70 $\pm$ 14	<0.10
25	131 $\pm$ 26	83 $\pm$ 3	13.2 $\pm$ 0.7	12.3 $\pm$ 1.0	81 $\pm$ 16	0.6 $\pm$ 0.1
30	152 $\pm$ 30	80 $\pm$ 4	16.9 $\pm$ 0.8	13.4 $\pm$ 0.8	77 $\pm$ 15	0.8 $\pm$ 0.2
35	129 $\pm$ 26	188 $\pm$ 8	43 $\pm$ 2	39 $\pm$ 2	25 $\pm$ 5	<0.10
40	228 $\pm$ 46	358 $\pm$ 12	84 $\pm$ 3	71 $\pm$ 3	40 $\pm$ 8	<0.10
50	154 $\pm$ 31	88 $\pm$ 4	12.6 $\pm$ 0.7	9.6 $\pm$ 0.9	41 $\pm$ 8	<0.10

**Fig. 5.** Vertical water profile of radionuclides in the ^{238}U series and stable Pb in a 60 m depth pit lake from central Sweden.

thus it was not considered further in this work.

The averages $\pm$ SD for the whole water column were 153 ± 32 , 129 ± 100 , 25 ± 26 and 22 ± 22 mBq/kg for ^{238}U , ^{226}Ra , ^{210}Pb and ^{210}Po respectively. And the total accumulated activity (in kBq/m²) was 9.3 ± 0.7 for ^{238}U , 7.5 ± 1.2 for ^{226}Ra , 1.3 ± 0.1 for ^{210}Pb and 1.4 ± 0.1 for ^{210}Po what represents around 20 kBq/m² of natural radionuclides in the water column.

Few studies can be found in the literature for comparison purposes: in this frame, Clulow et al. (1998) measured the distribution of ^{226}Ra with depth in five lakes from a watershed containing U mining and milling operations in Canada. Water was sampled at 0% (surface), 25%, 50%, 75% and 100% (bottom) of maximum depth of each lake and no changes of ^{226}Ra activity concentration with depth were found. This behavior could be explained because the maximum depth of the lakes (which ranged from 15 to 30 m) was not enough to develop stratification layers. ^{226}Ra activity concentrations were found in the range 10–100 mBq/L for the five lakes. In Salbu et al., 2013, studying the Kurday pit lake (an U former mine lake with 15.5 Bq/L of ^{238}U), ^{226}Ra was found with 191 mBq/L in surficial water. In the pit lake analyzed in this paper, ^{226}Ra ranged from 75 to 360 mBq/kg despite of not being in connection with U mining activities.

Concerning ^{210}Po in continental waters, typical activity concentrations range from 1 to 5 mBq/L in oxic water bodies while higher values, up to 17 mBq/L, can be found in seasonally anoxic ponds (IAEA, 2017). In former U mines, (Taboshar Pit lake) surface water with 5.6 ± 0.7 mBq/L of ^{210}Po were measured (Skipperud et al., 2013b) while in our work, ^{210}Po ranged from 7.5 ± 0.5 to 84 ± 3 mBq/kg (Table 2), again values above those found in literature.

The behavior of ^{226}Ra - ^{210}Pb - ^{210}Po chain has the same trend with depth: keeping constant activity concentrations in the oxic zone (0–30 m) to increase during the suboxic zone (30–40 m) to finally come back to previous values on the anoxic zone (40–50 m). However Pb has the opposite trend, decreasing when the suboxic zone was reached (See Fig. 5).

The increase in the activity concentrations of the radionuclides analysed found from 30 m down to the bottom will be easily understood in association to behavior of several metals that will be presented and discussed in coming paragraphs.

Practically secular equilibrium was found between ^{210}Pb and ^{210}Po (Fig. 6 Right) but a clear disequilibrium exist between ^{238}U and its progeny (Fig. 6 Left). These observations are extended from the surface down to the bottom of the pit lake (including anoxic layers). The well known mobility of U into aquatic media (Ivanovic and Harmon, 1992) in comparison with other elements/radionuclides from its series (Th, Pb, Po) facilitates this disequilibrium. The ratios of the ^{238}U progeny with ^{238}U are constant with depth during the oxic layer (above 30 m) and increase when the chemocline is reached, due to the input of ^{226}Ra and $^{210}\text{Pb}/^{210}\text{Po}$ in this layer in connection with some redox sensitive elements as will be discussed in section 3.3. Also disequilibrium was found between ^{226}Ra and ^{210}Pb (Fig. 6 Right). The $^{210}\text{Pb}/^{226}\text{Ra}$ ratio rises slightly with depth from 0.10 ± 0.01 at the surface, until 0.24 ± 0.01 –40 m depth to finally decrease to 0.14 ± 0.01 at the bottom.

At this point, it is interesting to remark that the data are suggesting that the deeper layers act as storage compartment with enhanced levels of radionuclides in pit lakes, fact that could be worth studying from the radioecological perspective for the potential risk posed to the environment.

In fact, under certain assumptions, from the analysis of the $^{210}\text{Pb}/^{226}\text{Ra}$ ratio it is possible to estimate the ^{210}Pb residence time ($\tau_{210\text{Pb}}$) in a water column. This residence time can be calculated (Niedermiller and Baskaran, 2019), by applying:

$$\tau_{210\text{Pb}} = \tau \left[\frac{\frac{^{210}\text{Pb}}{^{226}\text{Ra}}}{1 - \frac{^{210}\text{Pb}}{^{226}\text{Ra}}} \right] \quad (1)$$

where τ is the mean-life of ^{210}Pb (32.18 y). This equation can be used under the assumption that there is no net advective and/or diffusive input to the water column in the pit lake considered as one-dimensional box and also assuming that the scavenging is not reversible. In addition, it is assumed a low ^{210}Pb fallout effect and that no surficial inflow/outflow are connected with this pit lake affecting the analysed ratio.

Fig. 7 shows how this residence time ($\tau_{210\text{Pb}}$) rises with depth, resulting in 3.5 y at the surface, 5.8 ± 0.3 y in the oxic-and-deeper layer while the value rises to 9.4 ± 0.7 y in anoxic regions. A homogenous $\tau_{210\text{Pb}}$ in the range 10–25 m depth shows a complete mixture of this layer while the increment to 9.4 y in the anoxic layer (30–40 m depth) is compatible with a longer recirculation of the ^{226}Ra in this layer. It worth to mention that this former mine was operated between 1870 and 1987 and the pit lake formation takes several years to recover its previous water table level so this water body is not older than 20 years which is

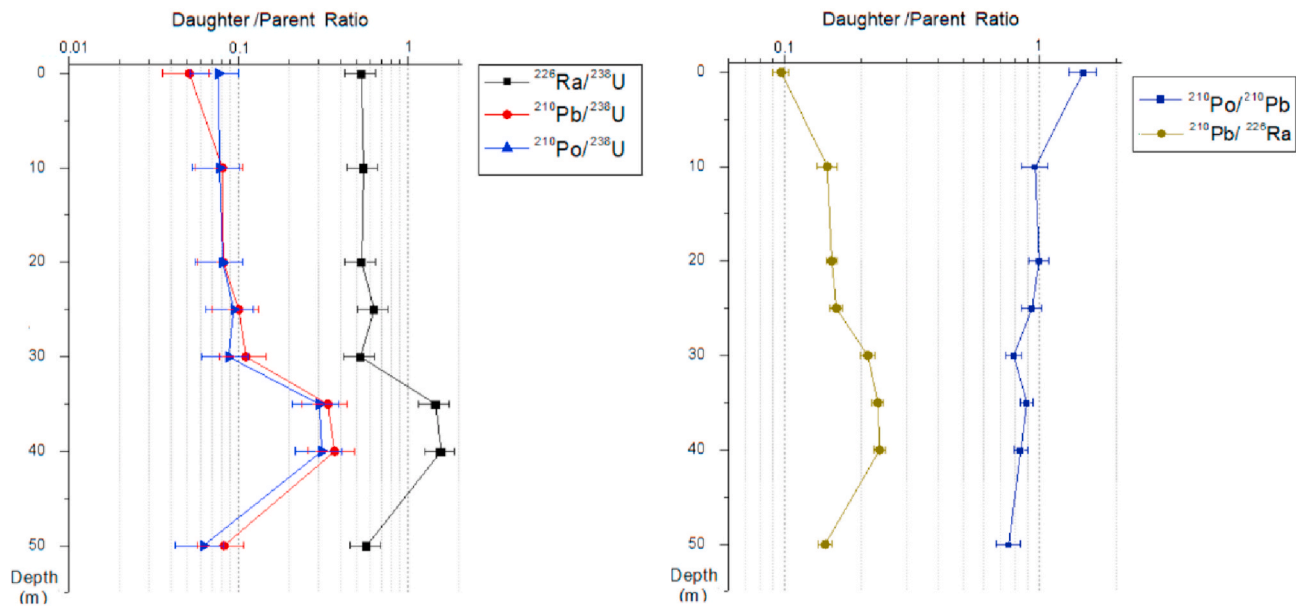


Fig. 6. (Right and left) Vertical profiles of daughter/parent ratios from different radionuclides in ^{238}U series radionuclides.

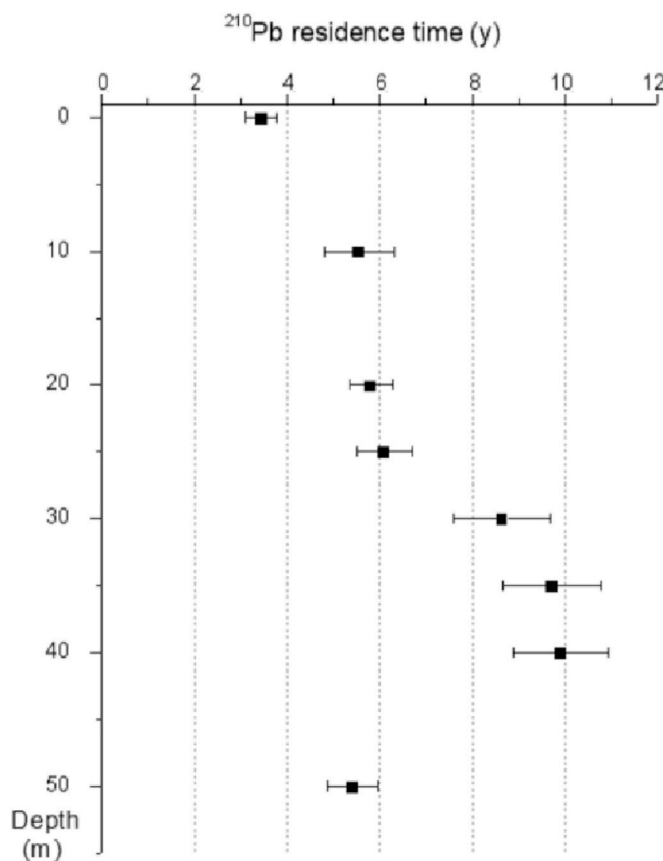


Fig. 7. ^{210}Pb residence time variation with depth in a pit lake.

compatible with the founded results.

In this point, it should be mentioned that both values of residence time: at the surface (0 m depth) and at the bottom (50 m depth) could be affected by boundaries conditions (i.e. air-water or water-sediments interface) not fulfilling the assumptions for Eq. (1) and, as a consequence, assessing inaccurate $\tau_{210\text{Pb}}$ results. At the same time, the values determined in the oxic zone can be slightly overestimated due to the

^{210}Pb fallout although the activity concentrations of ^{210}Pb in the water are clearly enhanced in relation to the found ones in natural lakes limiting the mentioned influence. On the other hand, in support of the $\tau_{210\text{Pb}}$ results we should remember that a ^{210}Po - ^{210}Pb equilibrium is found in all the water column ensuring that at least a ^{210}Po residence time of 2 y is achieved in the lake.

Reported values of ^{210}Pb residence time in natural lakes are in the range of 30–40 days or below (Talbot and Andren (1984); Benoit and Hemond (1987); Mudbidre et al., 2015), which are much shorter than the values found in this work. However, the pit lake under study is a closed water body without known inputs and output of surface water flows while the mentioned natural lakes were freshwater systems with flow through. In a wider context (marine environment), values in the range 15.8 ± 0.3 to 486 ± 98 y for ^{210}Pb residence time in the upper layers of the oceans (Niedermiller and Baskaran, 2019) are also reported in literature.

3.2.3. Relevance of the radiometrical characterization in pit lake water columns

The afore-mentioned conclusion that the accumulation of natural radionuclides can occur in deeper layers in pit lakes where stratification takes place, is a relevant finding that can be connected to some situations associated with this water bodies.

As an example, in May 2017 the water spill from an acidic pit lake (La Zarza) in southern Spain released 270000 m^3 of extremely acidic waters to the Odiel River (Olías et al., 2019). Surficial water in this pit lake was measured (Manjon et al., 2015), finding 1110 mBq/L, 1750 mBq/L, 390 mBq/L and 33 mBq/L for ^{238}U , ^{234}U , ^{230}Th and ^{210}Po respectively. If we assume that all the water column has a constant activity concentration with depth, this pit lake released 297 MBq, 475 MBq, 105 MBq and 9 MBq of ^{238}U , ^{234}U , ^{230}Th and ^{210}Po respectively to the Odiel River. This means that around 0.9 TBq of NORM radionuclides were released to the environment during this event (conservative assessment because neither ^{226}Ra nor ^{210}Pb were considered). But this assessment probably was underestimated if deeper layers of the pit lake contained higher concentration of NORM radionuclides.

The obtaining of non-uniform profiles in this type of lakes and no typical activities ratios between the radionuclides of the U series clearly evidence that the definition of average radioecological parameters for the whole lake has no meaning. The obtained results reinforce the idea of the need to investigate properly the peculiarities of different

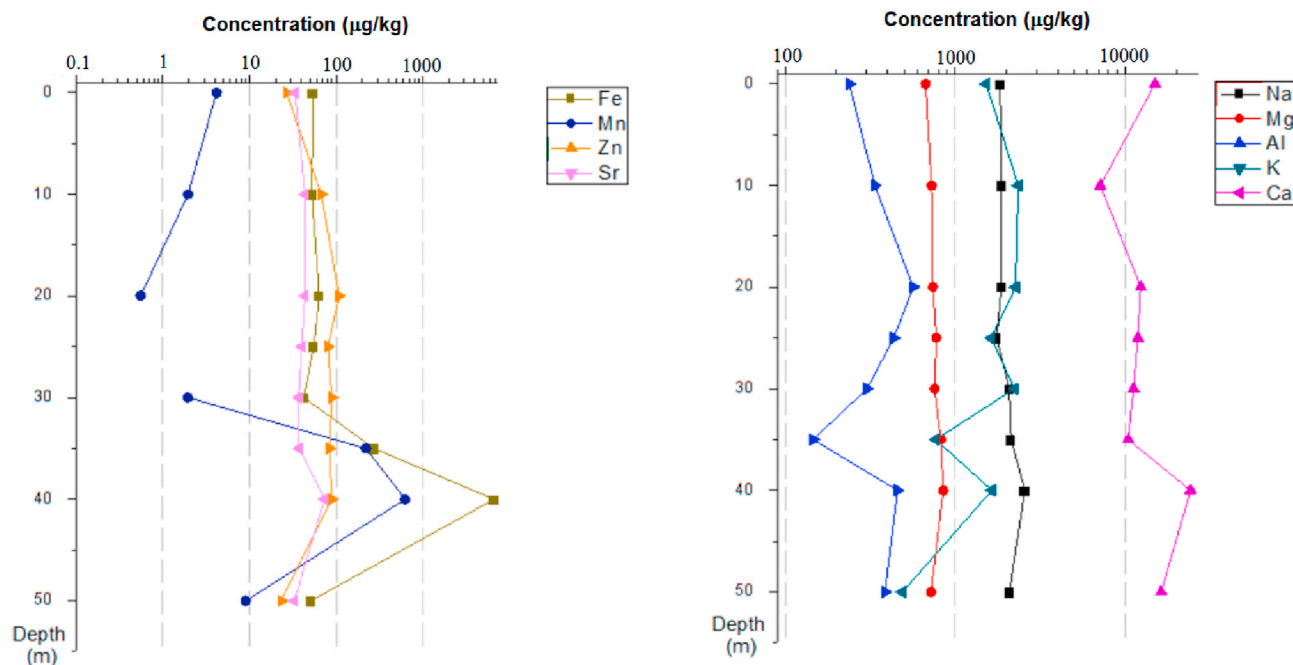


Fig. 8. The vertical distribution of selected elements in the studied pit lake. The concentration of all the measured elements are found in supplementary material, Table S2.

parameters like distribution coefficient (K_d), concentration ratio (CR), Bioconcentration Factors (BCF), etc ... which are essential in developing radioecological studies.

3.3. Metal content in lake waters

As expected, considering the pH values (6.5–7.0) and low SC values (100–200 $\mu\text{S}/\text{cm}$), the concentration of metals in the studied lakes is low (Fig. 8), with concentrations ranging from 7.1 to 25 mg/kg of Ca, 1.8 and 2.6 mg/kg of Na, 0.49 and 2.3 mg/kg of K, 668 and 849 $\mu\text{g}/\text{kg}$ of Mg, 54 and 665 $\mu\text{g}/\text{kg}$ of Fe, 145 and 565 $\mu\text{g}/\text{kg}$ of Al, 0.55 and 625 $\mu\text{g}/\text{kg}$ of Mn, 23 and 108 $\mu\text{g}/\text{kg}$ of Zn, 25 and 81 $\mu\text{g}/\text{kg}$ of Pb, 33 and 73 $\mu\text{g}/\text{kg}$ of Sr, 10 and 20 $\mu\text{g}/\text{kg}$ of Rb, 3.6 and 9.2 $\mu\text{g}/\text{kg}$ of V, 2 and 15 $\mu\text{g}/\text{kg}$ of Cr, 0.55 and 3.3 $\mu\text{g}/\text{kg}$ of Y, 0.2 and 2.9 $\mu\text{g}/\text{kg}$ of W, 0.30 and 2.6 $\mu\text{g}/\text{kg}$ of Ce, 0.09 and 0.56 $\mu\text{g}/\text{kg}$ of Gd, 0.08 and 0.31 $\mu\text{g}/\text{kg}$ of La. (Raw data to generate Fig. 8 are presented as Table S2 in Supplementary material). Following the same tendency as SC, higher concentrations were observed for most elements in the deeper layers of the pit lake than near the surface. For example, Na, Sr, Ca, Mg, Fe and Mn concentration peaked at 40 m depth, in coincidence with the anoxic layer of the pit lake. Other elements such as K, Al and Zn reached their maximum concentrations at shallower depths (between 10 and 20 m).

The increase in concentration for elements such as Ca, Mg, Sr or Na could be related to the dissolution of carbonates due to a decrease in pH values of lake waters. As can be seen in Fig. 3, a pH decrease is observed at around 30 m depth, which does not exactly fit with the increase in concentrations recorded at 40 m depth. This could be due to the dissolution of carbonates during the onset of the redoxcline (associated with a pH decrease) and subsequent diffusion of these enriched waters down to deeper layers of the lake.

On the other hand, the sharp increase in concentrations of Fe and Mn (30–35 m depth) is related to the reductive dissolution of Fe and Mn oxides. Both elements have a redox-sensitive behavior in aquatic environments, especially lakes, where seasonal redox changes in the hypolimnion result in the cycling of Fe and Mn (Balistrieri et al., 1992). Thus, the precipitation of Fe and Mn oxides is enhanced in lake waters under oxic conditions while the reductive dissolution of these mineral phases is observed during anoxic periods. The precipitation/dissolution cycles of

these mineral phases commonly lead to the incorporation/release of trace elements (Torres et al., 2013). In our case, this is reflected in the higher activity concentrations found in the upper region of the anoxic zone for ^{210}Po , ^{210}Pb and ^{226}Ra . The incorporation of ^{210}Po into Fe and Mn oxides and subsequent release upon anoxic conditions have been previously reported (Vaaramaa et al., 2003; Jones et al., 2015).

After applying a Pearson's correlation analysis, several relationships were found among physico-chemical parameters, elements and radionuclides (Table S3 in supplementary material) supporting previous comments. For instance, ^{238}U is highly correlated with its progeny ^{226}Ra , ^{210}Pb and ^{210}Po as expected, but also with the redox sensitive elements Fe (0.992) and Mn (0.828). Additionally Ca, Sr, Ba and Na shows high degree of correlations (in the range 0.660–0.999) with ^{238}U . The same observations can be seen for its progeny (which will be commented below in the PCA analysis). Pb only shows remarkable correlations with Y (0.788) and K (0.720) what confirms a complete different behavior (and so a different source) than ^{210}Pb isotopes.

This relationships, fit well with the results obtained from the PCA performed on samples (Fig. 9). The first component (F1) explains 47% of variance and appears to be related to the content of dissolved solids in lake waters. As can be seen in Fig. 9, depth and SC are located close each other, that is, the higher depth in the lake, the higher dissolved solids in waters. On the other hand, other variables such as DO and ORP are on the negative side of F1, reflecting an opposite behavior. This is clearly explained by the reductive dissolution processes of Fe and Mn oxides in the anoxic layers of the lake, leading to very low ORP values.

The second component (F2) explains 25% of variance and seems to be related with geochemical reactions that control the element mobility in lake waters.

Thus, several elemental groupings can be seen during the PCA (Fig. 9). On the one hand, elements associated to both carbonate (e.g. Ca, Mg, Sr, Ba or Na) and Fe and Mn oxide reductive dissolution (e.g. Mn, Fe, ^{210}Po , ^{210}Pb , or ^{226}Ra) are located close to each other, with low values of F2. On the other hand, some elements are located on the positive side of F2, exhibiting high values. Some elements such as Rb, Zn, Ce, Gd and Y could be related to the dissolution of Al hydroxides (Fig. 9). The relationship between Al minerals and rare earth elements and yttrium has been previously reported by Ayora et al. (2016).

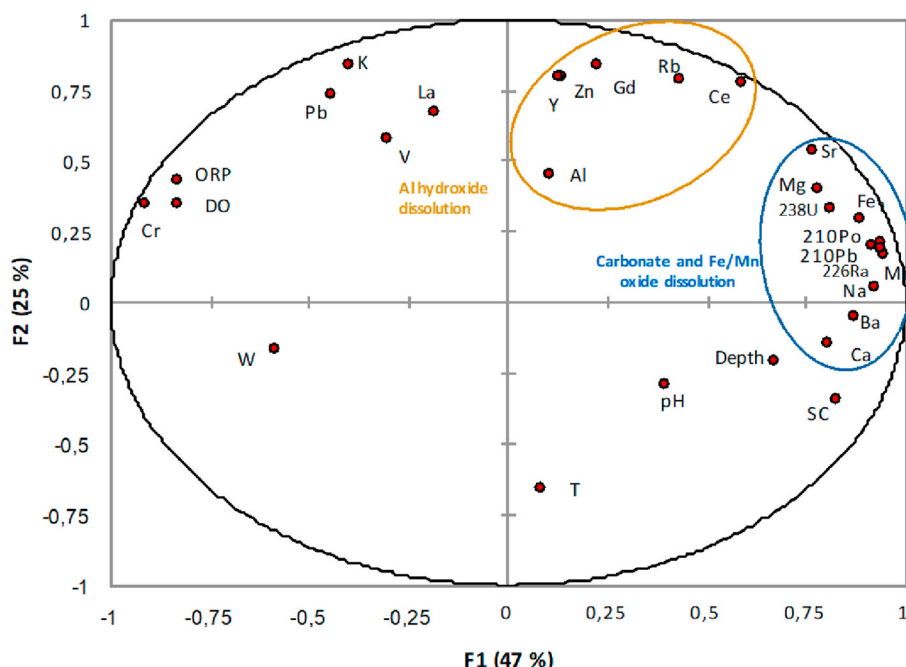


Fig. 9. Principal Component Analysis (PCA) on physico-chemical parameters measured in the pit lake.

Another interesting observation seen in the PCA plot is the different location of ^{210}Pb and Pb, corroborating a different origin of both isotopes. Thus, ^{210}Pb seems to be closely related to the concentration of Fe and Mn through their dissolution/precipitation cycle, while Pb seems not to be incorporated by these mineral phases. In fact, as can be seen in Fig. 9, Pb is located close to K, and other elements such as V and La.

4. Conclusions

A non-uraniferous 60 m depth pit lake with enhanced levels of ^{238}U radionuclides was selected for a water column characterization. The study was focused on NORM radionuclides ^{238}U , ^{226}Ra , ^{210}Pb and ^{210}Po , stable elements and water quality parameters from the water vertical profile.

Values of pH classify the pit lake as circum-neutral. An oxic layer from surface down to 30 m depth is characterized for low mineralization and constant concentration on elements and radionuclides. From 30 to 40 m a suboxic layer was identified where mineralization and radionuclides increased their concentrations. Finally an anoxic layer: 40–60 m depth (bottom) was found with a factor 2 higher mineralization level than oxic layer.

This former feldspar pit lake was found with enhanced levels of ^{226}Ra , ^{210}Pb and ^{210}Po (higher even than those found in some former U pit lakes). ^{210}Pb – ^{210}Po equilibrium and ^{226}Ra – ^{210}Pb disequilibrium were found from surface to bottom and variations with depth in these studied radionuclides were found and associated to redox conditions. This has allowed estimate residence times of ^{210}Pb and ^{210}Po in this water body characterized by the absence of water inflow and outflow. The residence time of ^{210}Pb in the pit lake water profile was assessed ranging mainly from 5.8 y in the oxic layer to 9.4 y in the anoxic layer.

Moreover, high correlation with elements associated to both carbonate (Ca, Mg, Sr, Ba or Na) and Fe and Mn oxide reductive dissolution were identified. Additionally, high correlation of some elements such as Rb, Zn, Ce, Gd and Y were connected with the dissolution of Al hydroxides. Finally a different behavior was observed between Pb isotopes in the water column: ^{210}Pb and stable Pb, the latter having a correlation coefficient of 0.72 with K.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvrad.2020.106384>.

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