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ASSESSMENT OF MAJOR AND TRACE ELEMENTS IN SOIL AND SEDIMENTS FROM OSAMU UTSUMI URANIUM MINE BY WDXRF

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ABSTRACT

From 1982 to 1995, the Brazilian Nuclear Industries (INB) extracted and processed uranium from the Osamu Utsumi mine, located in Caldas (Minas Gerais/Brazil). After the operations were suspended in the mine, INB was convened to meet national regulatory requirements for decommissioning the mine. Several studies have since been initiated in order to support a safe and responsible closure of the mine. In this context, this work aims to establish and validate a non-destructive methodology for quantitative simultaneous determination of major and minor constituents in soil and sediments from Osamu Utsumi uranium mine by wavelength dispersive X-ray fluorescence spectrometry (WDXRF). The method was validated in accordance to the criteria stablished by INMETRO (Brazilian's National Institute of Metrology, Quality and Technology). The precision and accuracy achieved are statistically comparable to the National Institute of Standards and Technology's standard reference material, SRM 2709a. The results showed significantly higher amounts of rare-earth elements and uranium in sediment samples, most likely because of the leaching process occurring in the pit's surroundings. This process is promoted by the acid mine drainage (AMD) that solubilizes the elements present in the tailings throughout the mine's area. The solubilized elements end up accumulating in the pit water and further depositing up in the sediment.

1. INTRODUCTION

The first uranium mining-industrial complex in Brazil was located on the plateau of Poços de Caldas (Minas Gerais, Brazil) under the name of “Osamu Utsumi”. The complex (CIPC) consists of an open pit, an ore crushing facility and a grinding plant for chemical processing [1]. The Brazilian Nuclear Industries (INB) had control of the operations in the mine, which initiated back in 1982 and lasted until the year of 1995. Approximately 44,56 million m^3 of mining waste was generated during this period. This waste was disposed in stacks over large areas surrounding the mining site, called “waste dumps” and “tailings beach”.

Acid mine drainage (AMD) results from the oxidation of sulfide minerals present in these wastes. This process releases H^+ ions, lowering the pH and creating conditions under which metals can be leached [2]. The effluent produced during this process contains dissolved metals in sulfuric acid [3]. The acidic environment favors the solubilization of radionuclides (uranium and thorium) and stable elements (such as manganese, iron, zinc, fluoride, etc.), increasing these elements’ concentration to levels that may exceed legal limits for direct launching into the environment. As a consequence, the plants and cover crops’ growth get inhibited, causing the erosion of the soil and an imminent threat of contamination of adjacent aquifers [4,5], since the chemical elements originated from the acid mine drainage (AMD) can reach up to hundreds of kilometers from the mining area. The effects can linger on for long periods of time, even after the cessation of the mining activities [6,7].

Nowadays, the mining and milling activities take place in Caetité (Bahia, Brazil), and has been since 1998. In 2004, INB signed an agreement to prepare and present a decommissioning plan in order to fulfil the requirements imposed by the Brazilian Institute of Environment and Renewable Natural Resources (IBAMA) and the National Nuclear Energy Commission (CNEN) requirements, both regulatory bodies in Brazil concerning environmental resources and nuclear, respectively. Because of this, actions have been taken to minimize the environmental impact such as: neutralization of the drained water (accumulated in the pit as a result of the AMD) and coating of the sterile heaps surface and waste rock piles with 30 cm layer of compact clay in order to avoid percolation of rain water through the piles [8].

Minding the extremely low pH of the water in the mine’s pit, a chemical treatment is being executed using calcium hydroxide, generating a dark alkaline sludge known as “DUCA” (calcium diuranate), which has been deposited in the pit’s borders for over 20 years and is mostly covered with acidic water now [9, 10,11]. After closing operations, water has been accumulating at the bottom of the mine over the years, covering the deposited DUCA.

Moreover, several studies were initiated in the attempt to support a safe and responsible closure of the mine, by monitoring the area and proposing alternatives for its remediation. In this context, this work aims to establish and validate a non-destructive quantitative chemical analysis methodology for simultaneous determination of major and minor constituents in soil and sediments from Osamu Utsumi uranium mine and vicinities by wavelength dispersive X-ray fluorescence spectrometry (WDXRF). Fast, accurate and easy to use, this technique requires a relatively simple sample preparation, allowing multi-element, non-destructive, analysis in a wide range of concentrations [12]. A standard reference material was used to perform the validation and the fundamental parameters method was applied for the quantitative determination.

2. MATERIALS AND METHODS

2.1. Sampling

The sampling of soil and sediment was conducted by technicians of the Nuclear and Energy Research Institute (IPEN/CNEN-SP) and INB throughout different sites of the mine-complex. All sampling sites are within the mine area and represent locations believed to be impacted the most by mining activities.

Surface soil samples were collected from different sites of the pit's surroundings and waste dumps (locally called "bota-fora" or "BF") using a stainless steel scoop after carefully removing the top layer of soil and debris to a desired sample depth of 10-20 cm.

One of the sediment samples was collected from the calcium diuranate deposit (DUCA), while the others were collected from the bottom of the pit's lake in 3 different points, using a Van Veen grab sampler. The site and location of each sample is shown in Table 1.

Each sample was placed into sterile labeled polypropylene bags and sealed hermetically for transportation to IPEN's Chemical and Environmental Analysis Laboratory (LAQA) at the Center for Chemistry and Environment (IPEN/CNEN-SP).

Table 1: Sampling sites and GPS coordinates

Sample ID	Sampling site	Location	
Soil 1	BIA	-21º57'27.8"S	-46º30'37.3"W
Soil 2	BF 4-1	-21º56'32.7"S	-46º29'19.3"W
Soil 3	BF 4-2	-21º56'27.0"S	-46º29'21.8"W
Soil 4	BF 4-3	-21º56'27.5"S	-46º29'23.9"W
Soil 5	BF 8-1	-21º57'23.6"S	-46º30'33.8"W
Soil 6	BF 8-2	-21º57'14.4"S	-46º30'33.1"W
Soil 7	BF 8-2	-21º56'48.4"S	-46º30'21.5"W
Soil 8	DUCA-2 TRINE	-21º56'55.8"S	-46º30'12.2"W
Soil 9	TRINE-3	-21º56'48.9"S	-46º29'50.4"W
Sediment 1	DUCA-1	-21º57'24.48"S	-46º30'29.90"W
Sediment 2	Mine Pit-1	-21º56'44.1"S	-46º29'52.5"W
Sediment 3	Mine Pit-2	-21º56'46.4"S	-46º29'57.7"W
Sediment 4	Mine Pit-3	-21º56'50.0"S	-46º30'06.3"W

BIA: captation basin of effluent water from waste dump 8; BF: waste dump (locally called "bota-fora"); DUCA: calcium diuranate; TRINE: site that surrounds the mine's lake.

2.2. Sample preparation

After sampling, soil and sediment samples were subjected to oven drying at 105 ± 5°C, according to the certificate supplied with NIST's standard reference material 2709a (San Joaquin Soil).

Each sample was crushed and homogenized in an agate mortar in order to achieve a particle size between 74 and 105 µm. Approximately 2.0 grams of each sample was pressed into a 25.00 ± 0.01 mm diameter and 5.0 ± 0.2 mm thick disc using a hydraulic press and applying a pressure of 20 MPa . 2 s^{-1} on a boric acid (H_3BO_3 P.A.) basis, which has been previously compressed at 100 MPa . 2 s^{-1}.

2.3. Instrumental parameters

The experiments were carried out using a RIGAKU Co (Tokyo, Japan) wavelength dispersive X-ray fluorescence spectrometer, model RIX 3000 with a Rh-anode X-ray tube, a 75 µm Be window, a 60 kV maximum acceleration voltage generator, a NaI(Tl) scintillation detector and a gas-flow proportional counter. The fundamental parameters (FP) method was applied for correction of the absorption/excitation effects. The parameters such as excitation, emission line, divergence slit, diffracting crystal, type of detector, scan counting time, and Bragg's positions are shown in Table 2.

Table 2: Measurement conditions for WDXRF - Excitation: 50 kV x 50 mA

Elements	Emission line	Divergence slit (µm)	Diffracting crystal	Detector	Step (^{o}) / Time (s)	Bragg's positions (^{o})
Na	Na-Kα	560	TAP	FPC	0.05 / 1.0	52.000-58.000
Mg	Mg–Kα	560	TAP	FPC	0.05 / 1.0	42.000-48.000
Al	Al-Kα	560	PET	FPC	0.05 / 1.0	140.000-147.000
Si	Si-Kα	560	PET	FPC	0.05 /0.4	106.000-112.000
P	P-Kα	560	Ge	FPC	0.05/0.4	138.000-144.000
S	S-Kα	560	Ge	FPC	0.05/0.4	108.000-114.000
Cl	Cl-Kα	160	Ge	FPC	0.05/1.0	90.000-96.000
K	K-Kα	560	Ge	FPC	0.05/0.4	60.000-64.000
Ti-U	Kα	560	LiF(200)	SC	0.02/0.2	5.000-90.000

TAP thallium acid phtalate, PET pentaerythritol, LiF lithium fluoride, Ge germanium, SC scintillation detector, NaI(Tl): FPC gas-flow proportional counter

2.4. Fundamental parameter method

The fundamental parameter (FP) method was applied for the quantitative determination using the 2theta scan mode of the spectrometer's software.

This method employs mathematical algorithms to correct inter-element of coexisting elements (absorption and enhancement of X-rays and overlap of peaks) through the measure of the intensity of each element's emission line and the tabulated values of the main fundamental parameters, such as the primary spectral distribution (source), the photoelectric and the mass absorption coefficients, fluorescence yields and others [13].

Quantitative analyzes performed through the FP method don't necessarily require the usage of certified reference materials. However, the reliability increases when the parameters that make up the mathematical expression are obtained by appropriate and traceable standards. The calculations involve two underlying steps: calibration and prediction.

In the calibration step, the FP equation is employed to predict the characteristic intensities of the calibration standards' emission lines. The calculations are performed specifically for the instrument through which the measurements are obtained, since the PF's equation considers geometry aspects, source and instrumental conditions. The calibration takes into consideration the theoretically calculated intensities and the measured intensities, which are corrected for each characteristic line. This correction is acquired through the angular coefficient, experimental net intensities versus the calculated relative intensities, which correspond to the proportional factor used in the correction[14].

In the predicting step, it is necessary to estimate the approximate composition of the sample first. Typically, the detected emission lines' relative intensity corresponding to each element in the matrix is considered, assuming that the total emission pertains to a composition of 100% (or another total value, if the minor constituents are ignored[14].

From this equation, the intensities that should be observed for the assumed composition are software-calculated. They are compared to the measured values, then the assumed composition is adjusted and a new set of expected intensities is calculated. This interaction process is automatically repeated until the assumed composition provides an X-ray intensity that corresponds to the measured value at a significance level of 0.05. The composition that successfully meets this relationship becomes the result of the analysis [14, 15].

2.5. Methodology evaluation

The methodology was validated in terms of precision and accuracy through statistical tests suggested by INMETRO's document *DOQ-CGCRE-008* [16]. The data were obtained for 3 replicates of each sample and 7 measurements for each replicate, adding up to a set of 21 measurements for each element of NIST's standard reference material, SRM 2709a, *San Joaquin Solo*.

The Chauvenet test was applied for the detection of the outliers, Eq. 1 [17].

$$|Xi - \bar{X}| > Kn * s \tag{1}$$

Where Xi is a measured value, $\bar{X}$ is the average value, Kn is the Chauvenet's coefficient and s is the standard deviation.

The limit of quantification (LoQ) for the certified elements was calculated for a 95% confidence level, according to Eq. 2 [18].

$$LoQ = 2 * \sqrt{\frac{\sum_{m=1}^{n}(C_m - \bar{C})^2}{n-1}} \tag{2}$$

Where, C_m is the measured value, $\bar{C}$ is the average value and n is the number of replicates.

The precision was evaluated through the relative standard deviation (%RSD) and the acceptability was verified using the equation of Horwitz, in which the HORRAT's (HO_R) values fit more accordingly Eq. 3 [16].

$$HO_R = \frac{DPR\%_{experimental}}{DPR\%_{previsto\ da\ equação\ de\ Horwitz}} \tag{3}$$

The accuracy was evaluated through the Z-score test, according to Eq. 4 [16].

$$Z = \frac{(\bar{X}_{Lab} - \bar{X}_{CRM})}{\sqrt{U_{Lab}^2 + U_{CRM}^2}} \tag{4}$$

Where, Z is the test value, $\bar{X}_{Lab}$ is the experimental average, $\bar{X}_{CRM}$ is the CRM's true value, U_{Lab}^2 is the experimental variance and U_{CRM}^2 is the variance obtained for the CRM.

3. RESULTS AND DISCUSSION

3.1. Quality Control

In Table 3, certified and determined values, RSD %, HO_R, RE %, LoQ, and Z-score for CRM 2709, from NIST are presented.

Table 3: Certified and determined values, RSD %, HO_R, RE %, LoQ, and Z-score for CRM 2709

Elements	Xcert ± σ	Xdeter ± σ	RSD %	HO_R,	RE %	Z	LoQ
Na (%)	1.16±0.03	1.09±0.02	1.8	0.9	6.2	-2.0	0.04
Mg (%)	1.51±0.05	1.63±0.04	2.5	1.3	-8.1	2.0	0.07
Al (%)	7.50±0.06	7.7±0.2	2.6	1.3	2.8	1.1	0.4
Si (%)	29.66±0.23	29.2±0.6	2.1	1.1	1.6	-0.7	1.2
P ($\mu g\ g^{-1}$)	620±50	700±20	2.9	1.5	-12.3	1.5	32
S ($\mu g\ g^{-1}$)	890±20	940±30	3.2	1.6	-5.1	1.3	54
K (%)	2.03±0.06	2.13±0.07	3.3	1.7	-4.9	1.0	0.15
Ca (%)	1.89±0.05	1.95±0.03	1.5	0.8	-3.4	1.1	0.05
Ti (%)	0.342±0.024	0.34±0.01	2.9	1.5	1.7	-0.2	0.03
Fe (%)	3.5±0.1	3.4±0.1	2.9	1.5	1.7	-0.5	0.1
V ($\mu g\ g^{-1}$)	112±5	101±5	5.0	1.3	9.7	-1.5	11
Cr ($\mu g\ g^{-1}$)	130±4	142±5	3.5	0.9	-8.9	1.8	10
Mn ($\mu g\ g^{-1}$)	538±17	535±36	6.7	1.7	0.6	-0.1	73
Ni ($\mu g\ g^{-1}$)	88±5	95±4	4.2	1.1	-7.4	1.0	8
Cu ($\mu g\ g^{-1}$)	34.6±0.7	37±2	5.4	1.4	-8.1	1.3	4
Zn ($\mu g\ g^{-1}$)	106±3	104±7	6.7	1.7	1.7	-0.2	14
*Rb ($\mu g\ g^{-1}$)	96	85±3	3.5	0.9	11.8	***	6
Sr ($\mu g\ g^{-1}$)	231±2	230±10	4.3	1.1	0.4	-0.1	19
*Zr ($\mu g\ g^{-1}$)	160	177±8	4.5	1.1	-10.8	***	15
Ba ($\mu g\ g^{-1}$)	968±40	990±44	4.4	1.1	-2.3	0.4	88
Pb ($\mu g\ g^{-1}$)	18.9±0.5	18±1	5.6	1.4	2.4	-0.5	2

* ≡ Noncertified Values

The results obtained for the certified reference material showed that the method's precision (RSD%, n=7) ranged from 1.5 to 6.7%. The Horwitz ratio (HorRat or HO_R) was the parameter used to indicate the acceptability of the method, with respect to among-laboratory precision. Since the calculated values for all the elements are below 2, the method is able to generate results with satisfactory precision [16].

The accuracy was evaluated in terms of relative error (RE%), which ranged from 0.4 to 12.3%. The acceptability of these values, assessed using the Z-score test, showed that the calculated values for all elements are ≤ 2, indicating that the obtained results are in good agreement with the certified values [16].

The limits of quantification calculated for the major constituents ranged from 0.04 (Na) to 1.2% (Si) and, for the minor constituents, from 2 (Pb) to 73 µg g^{-1} (Mn). Finally, the results show that the proposed methodology is statistically suitable and, therefore, satisfactory for the determination of major and minor constituents in soil and sediment samples, as well as similar matrices.

3.2. Soil samples

The results obtained by WDXRF analysis revealed the major elements found in the soil samples from Osamu Utsumi mine (Fig 1).

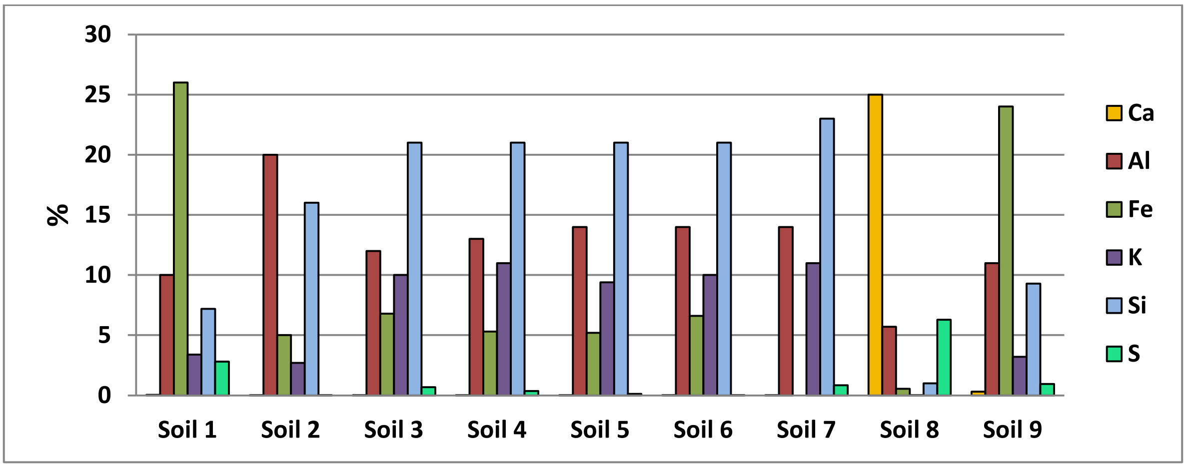

Figure 1: Major constituents in soil samples

Samples 2, 3, 4, 5, 6 and 7 (Group 1) are constituted predominantly of Si (approx. 15-23%) and Al (approx. 12-20%). According to Table 1, these samples were all collected from the waste dump, showing some consistency with each other regarding their major constituents.

Fe and Al are the main elements present in samples 1 and 9 (Group 2), evidencing a similarity between the sample collected from the mine's pit (Soil 1) and the one collected in TRINE-3 (Soil 9).

Ca is found as the main constituent of the matrix in sample 8 (approx. 25%), which is consistent to the nature of the sample. According to Table 1, "Soil 8" was collected from a calcium diuranate deposit (DUCA), resulting from the treatment of the acidic waters from the mine's pit.

Taking into account the high concentrations of Fe (20-25%) found in samples 1 and 9, it is noticeable that the leaching process must be more accentuated in the sampling sites from which the samples from the Group 2 were collected.

Other 21 elements were evaluated, but since rare-earth elements were found in significant amounts in all soil samples, especially Ce, La and Nd, they were grouped apart in Fig. 2.

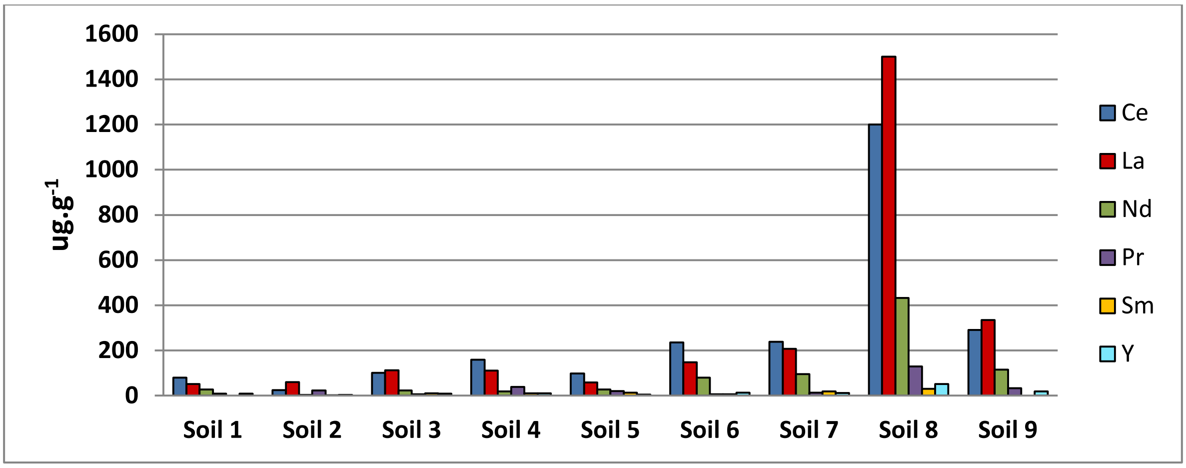

Figure 2: Rare-earth elements in soil samples

The highest amounts of Ce, La and Nd are found in “Soil 8”, showing that these elements tend to concentrate in the DUCA deposit as a result of the neutralization process applied to the acidic pit water. Ce concentration in “Soil 8” (1200 µg g^{-1}) is up to 48 times higher than in “Soil 2”, the sample which presented the lowest amount of this element (25 µg g^{-1}). The average Ce concentration for samples 1, 2, 3, 4, 5, 6, 7 and 9 was of 153.5 µg g^{-1}. The concentration of La found in “Soil 8” was of 1500 µg g^{-1}, whereas the average concentration found for the remainder of the samples was 135.6 µg g^{-1}. For Nd, the average concentration for all samples, except “Soil 8”, was 46.5 µg g^{-1}, while “Soil 8” registered a 433 µg g^{-1} concentration, i.e., approximately 10 times higher.

Fig. 3 shows the relative concentrations of the most significant minor constituents of each soil sample.

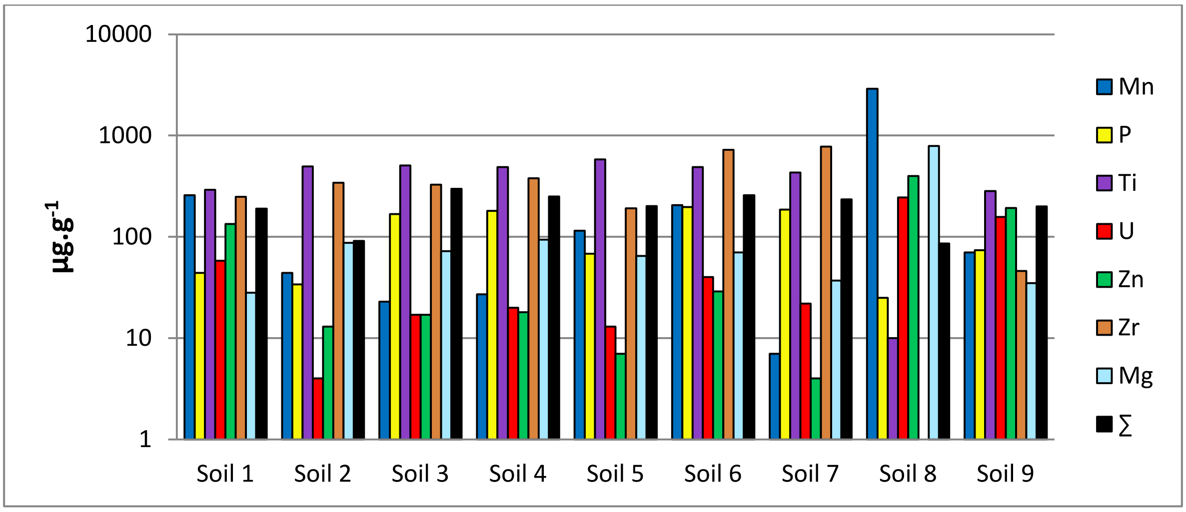

Figure 3: Minor elements in soil samples

Where “Σ” is the sum of the results obtained for 10 minor elements (Cl, Ga, Na, Nb, Ni, Pb, Rb, Sr, Sr, Th and V), which individual concentrations were too low to be compared with the other elements.

Evaluating Fig. 3, U is found to be in comparably higher concentrations in samples 8 and 9 (above 100 µg g^{-1}), while Soil 8 presents the highest concentration of Mn (2900 µg g^{-1}) among the studied samples, supporting that some elements may be concentrated in the DUCA deposit.

3.3. Sediment samples

Fig. 4 shows the results obtained by WDXRF analysis for the sediment samples.

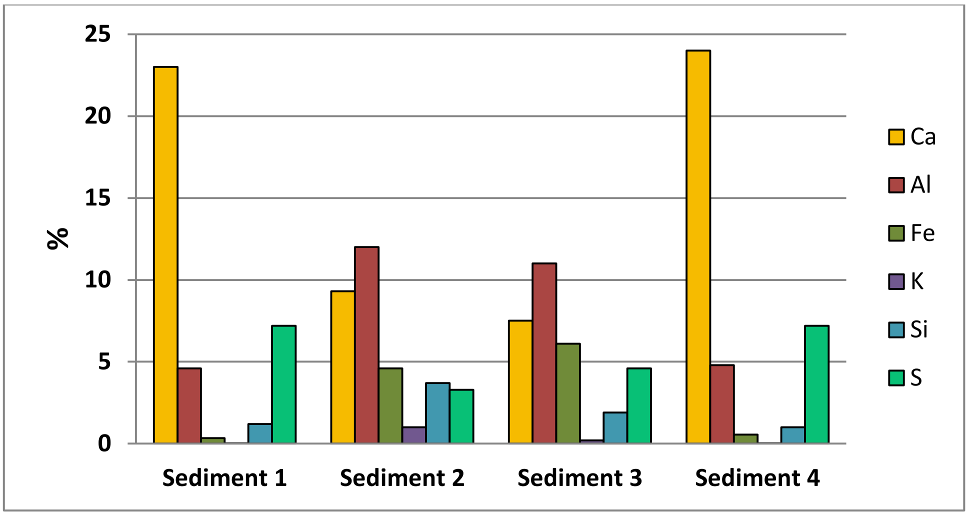

Figure 4: Major constituents in sediment samples

Samples 1 and 4 present Ca as the main constituent (23% and 24%, respectively), indicating that "Sediment 4", which was collected from the site designated as "Mine Pit-3", has a chemical similarity to the sample "Sediment 1", corresponding to the calcium diuranate (DUCA). Due to neutralization processes of the acid drainage water, calcium diuranate precipitates and is placed in the pit's borders (as DUCA). Leaching processes dilute some of the calcium, which is drained back to the mine's pit and further precipitates as $CaCO_3$. This explains the elevated calcium levels in the sediment sample 4.

This concentration process might constitute a potential challenge to the decommissioning of the mine, once some elements may be resolubilized and, thus, concentrated in the pit water by acid leaching occurring in the DUCA deposit. This, in turn, could potentially become a magnification cycle, increasing the availability of these elements in the mine, since the water will be treated again by neutralization processes and be deposited as calcium diuranate, which will undergo further leaching and resolubilization and so on.

Samples 2 and 3 exhibit a matrix composed of mostly Al, Ca and Fe. They were both collected from inside the mine's pit. Fe is significantly higher in these samples (4.6% for "Sediment 2" and 6.1% for "Sediment 3"), compared to samples 1 and 4 (0.35% and 0.55%, respectively), most probably because of the leaching process that happens in the pit's surroundings, which result in water deposits rich in solubilized Fe.

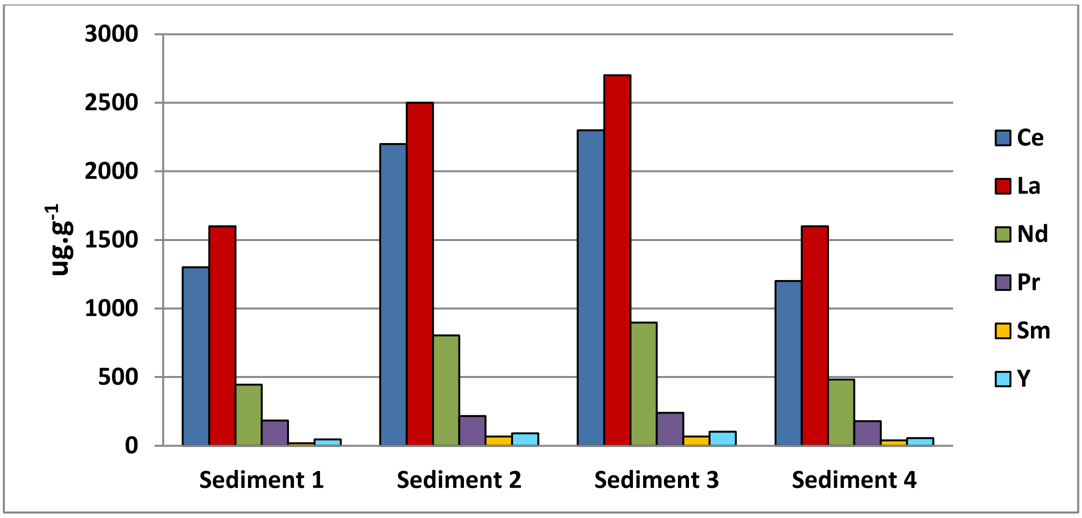

Figure 5: Rare-earth elements in sediment samples

Rare-earth elements were also found in significant amounts in all sediment samples, especially Ce, La and Nd, as seen in Fig. 5. The concentrations are considerably higher compared to those found in the soil samples, indicating that these elements are not only prone to settle in the bottom of the pit's lake, but also concentrate over time.

Fig. 6 shows the relative concentrations of the most significant minor constituents of each sediment sample.

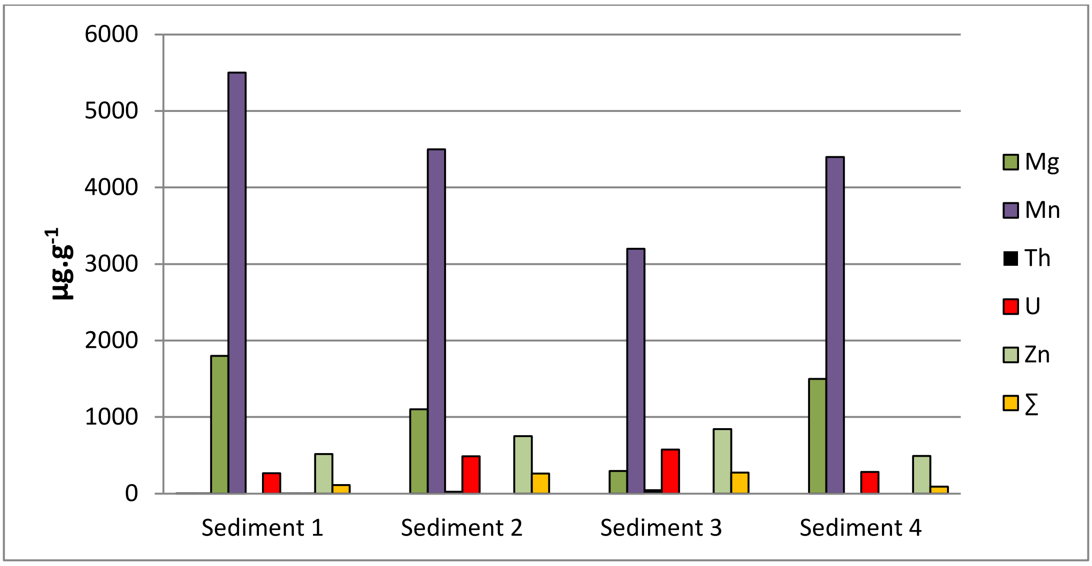

Figure 6: Minor elements in sediment samples

Where "Σ" is the sum of the results obtained for 8 minor elements (Na, Nb, Ni, P, Pb, Sr, Ti and Zr), which individual concentrations were too low to be compared with the other elements.

Samples 1 and 4 present U at an average concentration of 275 μg g^{-1} while in samples 2 and 3, U is present in an average concentration of 532 μg g^{-1}, i.e, practically the double. Mn is found in high concentrations in all samples, ranging from 3200 to 5500 μg g^{-1}.

Fig. 7 shows the comparative distribution of the rare-earth elements among the soil and the sediment samples.

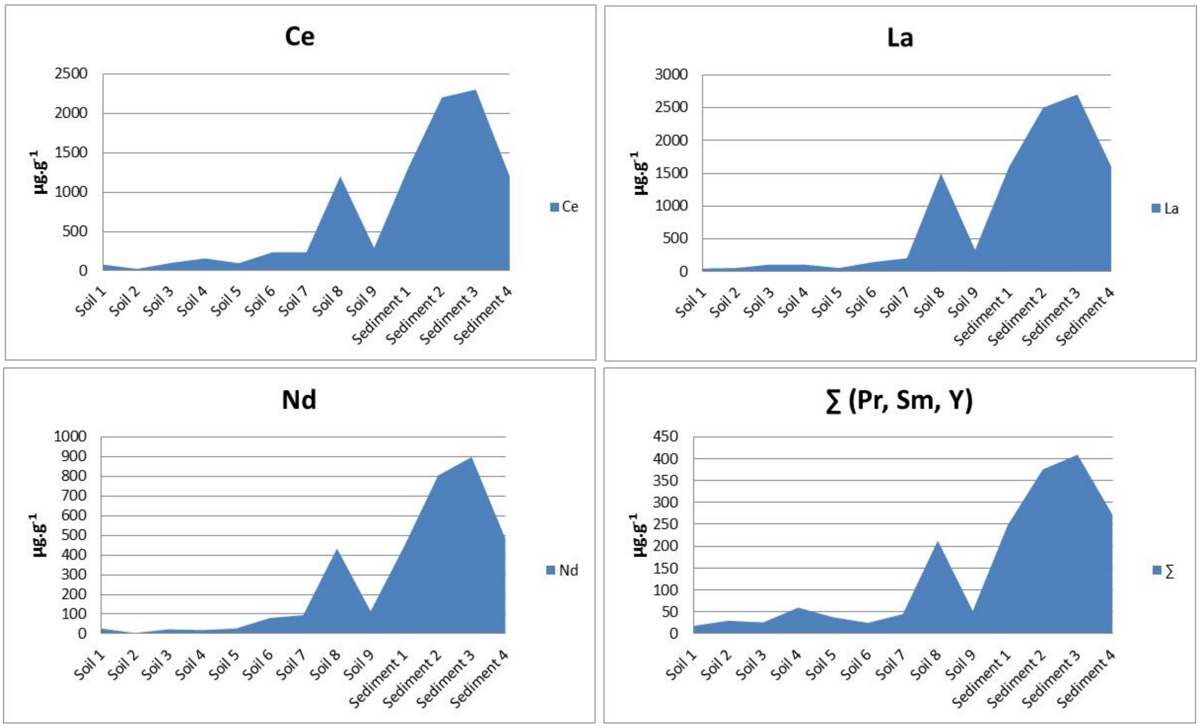

Figure 7: Distribution of rare-earth elements among soil and sediment samples

Fig. 8 shows the same distribution for uranium, given that U is considered a monitoring element of the mine’s activity.

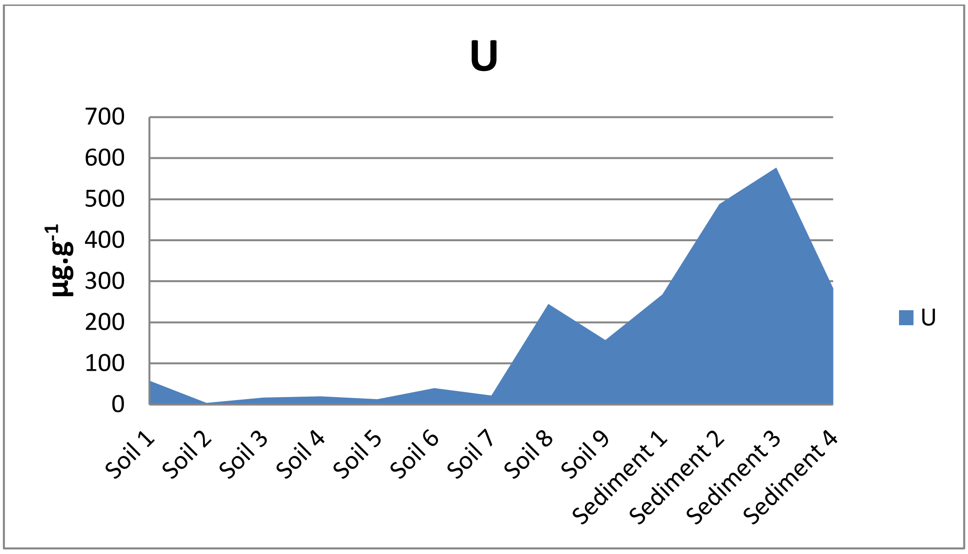

Figure 8: Distribution of uranium among soil and sediment samples

From Fig. 7 and Fig. 8, it becomes evident that U and rare-earth elements are likely to concentrate in the sediment. This probably occurs because of the solubilization of these elements where the waste-dumps are thrown, promoted by the acid mine drainage (AMD). The solubilized elements accumulate in the acidic water and further end up depositing up in the bottom of the mine’s lake.

Taking this under consideration, special attention should be directed to the disposal of the mining wastes and tailings throughout the mine. Acid mine drainage (AMD) promotes the resolubilization of many elements which get drained back to the pit lake. This, in turn, promotes the concentration of these elements in the water, i.e., their availability increases and they may be precipitated as calcium diuranate during neutralization of the water (one of the chemical treatments applied to the water). This precipitate is then deposited around the pit as the “DUCA” deposit. The elements present in the DUCA become susceptible for leaching again, returning to the pit water in a cycling process.

Contaminated water in the pit lake can impact down-gradient groundwater quality. The concentration of metals and other contaminants in the pit may, through evaporation, impact migratory birds and terrestrial wildlife.

4. CONCLUSION

The quantitative determination of major and minor constituents in soil and sediments from Osamu Utsumi uranium mine was carried out by WDXRF technique using the fundamental parameter method. This methodology was successfully validated in agreement with INMETRO’s requirements using NIST’s standard reference material SRM 2709, demonstrating the ability to satisfactorily produce precise and accurate results. The levels of uranium and rare-earth elements were found to be significantly higher in sediment samples than in the soil samples as a result of acid leaching processes in the pit’s surroundings. These results are believed to provide an initial insight of the mechanisms occurring in the mine and how they may influence the chemical composition of the soil and sediment.

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