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Remediation of Caldas site by monitored natural recovery

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ABSTRACT

Acid mine drainage (AMD) is one of the main environmental issue caused by oxidation of pyrite (FeS_2) when exposed to atmospheric conditions during mining. In Brazil, one of the places where AMD occurs is an old uranium mine in Minas Gerais State. The acid waters contain radionuclides and other metals that are precipitated with the addition of lime. Due to the inefficiency of the water treatment plant, part of the precipitate containing the metals overflows from the settling tanks and reach the water reservoir of Indústrias Nucleares do Brasil – INB. The multiplicity of interactions that can occur between the extremely fine particles of the precipitate and the sediments of the reservoir requires a broader approach in order to understand the fixation and/or transport of the metals. In this work the natural recovery approach is reviewed and a chemical and radiochemical characterization of the sediments are presented. Uranium and thorium were determined by spectrophotometry, ^{226}Ra, ^{228}Ra and ^{210}Pb by gamma spectrometry and Zn and Mn by ICP-OES. A panorama of the contamination is shown in different maps by using ArcGis program. Twenty-six sediment samples were collected in the reservoir and a bathymetry survey by sonar was performed to determine the thickness of the sediment layer. Most of the samples have presented activity concentrations of uranium and thorium higher than the background values. Further investigation will assess the potential mobility and bioavailability of contaminants and the role of bacterial sulfate reduction in the immobilization of these contaminants.

Keywords: sediments, acid mine drainage, uranium, zinc.

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1. INTRODUCTION

Mining is a strategic activity in the world economy and has its importance recognized for the development of Brazil, which is one of the main exporters of several minerals. However, if appropriate environmental practices are not adopted, mining activities could be sources of inorganic contamination [1]. One environmental problem of great concern is acid mine drainage (AMD). It is caused mainly by oxidation of pyrite (FeS_2) when exposed to air and water during the mining process causing the generation of acidity (H^+). As an aggravating factor, this process can be catalyzed by bacteria activity that greatly accelerate acid producing reactions.

The acid effluent is characterized by low pH and high content of sulfate and dissolved metals [1, 2, 3, 4]. Due to its high capacity to leach the elements present in the ore it can contaminate surface water and groundwater. AMD sources include waste rock piles, ore stockpiles, tailings storage facilities and tailings dams, open cuts, underground mines and heap and dump leach piles. This problem is not exclusive to mining activities and can occur in any operation that results in a large movement of soil and rocks containing FeS_2. The sulfide minerals responsible for AMD can be found in coal or nickel, lead, zinc, copper, uranium, gold and silver ores. The AMD occurrence can be predicted by determining the minerals that constitute the ore and their potential risks associated to acid generation. The focus should be on prevention or minimization rather than on treatment [3].

In Brazil, AMD occurs in a uranium mine in Caldas Municipality, Minas Gerais State, which is under decommissioning. Before being discharged to the environment, the levels of metals and sulfate present in the AMD are reduced by raising the pH with lime. However, part of the precipitate containing Zn, Mn, Pb, U and Ra, reaches a water reservoir that belongs to Indústrias Nucleares do Brasil – INB, leading to a concern about the sediment contamination and the migration of the metals to the environment.

The reservoir under study is located in *Antas creek,* downstream the water treatment plant, with a drainage area of approximately 50 km², 3.5 km length and 250 m of average width. During mining activities, it was used to supply water to the ore treatment plant from INB. Currently, the treated effluent flows to the reservoir and previous study shows that the sediments are contaminated with metals, including uranium, whose contents are above the background levels [4]. The study investigated only 4 points and not all the radionuclides were investigated. So, a deeper investigation is necessary as the contaminants can be toxics to the environment, due to the deleterious or adverse biological effect caused by chemical, physical or biological agents. According to the Environmental Protection Agency (EPA) [5], contamination is the introduction of harmful or hazardous matter into the environment, where it should not be or it is at concentrations above background.

The recognition of the environmental risks of AMD has led to the development of several techniques to minimize their impact on the ecosystem. Although conventional neutralization systems through the addition of alkaline reagents are the most commonly used, systems containing sulfate-reducing bacteria are also employed for AMD treatment [1, 2, 3]. Effective sediments remediation actions must consider the relative importance of these two processes, sulfide oxidation and bacterial sulfate reduction [6].

This study investigated the sediments of one water reservoir, highly affected by uranium mining activities, in order to determine the capacity of the system to undergo natural attenuation. For that, a chemical and radiochemical characterization of the sediments as a preliminary assessment of the main radionuclides was carried out. The thickness of the sediments was also determined by bathymetry survey and data obtained were treated by using ArcGIS program.

1.2. Monitored Natural Recovery in Site Remediation

EPA published in 2005 a document that provides technical and policy guidance for managing contaminated sediment sites [7]. According to this document, monitored natural recovery (MNR) is a choice for the remediation of contaminated sediment that generally uses continuous naturally occurring processes to contain, destroy, or decrease the bioavailability or toxicity of contaminants in sediments. Some of the natural processes result in the lowering of risks, however, some of them may increase or change risks to other places or receptors. MNR may use processes that include physical, biological, and chemical mechanisms acting together to reduce the risk posed by the contaminants. Depending on the contaminants and the environment, the reduction of the risks may occur in different ways, e.g., the contaminant may be changed to a less toxic form through mechanisms such as biodegradation or abiotic transformation; the mobility and bioavailability of the contaminants may be reduced through sorption or other processes that bind contaminants to the sediment matrix [7]. These cited mechanisms are the most important ones for the present investigation.

In most cases, the main advantages of MNR are its relatively low implementation cost and its non-invasive nature. While costs of characterization and modeling can be high, in MNR, they are more associated with just monitoring. Other positive facts may include no needs for infrastructure, therefore, becoming much less disruptive for communities than dredging or in-situ capping [7].

MNR limitations can include the permanence of the contaminants in place and its slow reduction of risks in comparison to active remediation processes. Moreover, there is risk of contaminants re-exposure. Uncertainties usually related to MNR include the incapability of predicting future sedimentation rates in dynamic environments and of predicting contaminant flux rates through stable sediments [7].

The success of MNR as a risk decreasing mechanism mostly depends on the understanding of the dynamics of the contaminated environment and the destination and mobility of the contaminant in that location. Chemical processes in sediments are very important for metals. The chemical state of metals in the sediments is ruled by many environmental variables that influences their mobility, toxicity and bioavailability. Much of the current knowledge of the role of chemical processes in risk control is focused on the important geochemical changes that come from changes in the redox potential and that may have influence in the bioavailability of metal and metal organic compounds. The formation of biogenic metal sulfides, under reducing conditions, can frequently and effectively control the risk of metal contaminants if the appropriate environmental conditions are sustained. This process produces alkalinity and causes the refixation of sulphur as sulphide minerals in the sediment matrix. Besides that, many chemical processes in sedimentary environments are affected by the biological community as well [7, 8].

For the assessment of potential bioavailability of metals in river sediments, a traditional method is the AVS/SEM which determines the acid volatile sulfide (AVS) and the metals that are dissolved during the acidification step (Simultaneously Extracted Metals—SEMs) [8, 9]. Sulfate from the AMD can be reduced to sulfide due to bacterial action. These sulfides formed by microbial reduction of SO_4^{2-} are consisted mainly of free sulfides, FeS, and Fe_3S_4, as well as relatively low solubility metal sulfides such as copper, nickel, zinc, cadmium, and lead [10, 11, 12].

The literature reports three criteria to express the relationship between AVS and metal toxicity: (i) the difference between SEM and AVS ($\sum$SEM − AVS), (ii) the ratio of SEM to AVS ($\sum$SEM/AVS), and (iii) the SEM to AVS difference normalized by the fraction of total organic carbon (TOC) in a sediment ((SEM − AVS)/TOC). Normalization by TOC is justified by the fact that organic matter is intrinsically related to the bioavailability of the metals [10, 11, 12], once the organic matter is an important source of extra binding capacity, forming less toxic complexes.

Other studies have shown that the toxicity to benthic organisms does not occur when the concentration of AVS is greater than the sum of simultaneously extracted metals SEM from the sediment. This assumption is based upon the low solubility of the metal sulfides which are removed from the soluble fraction by precipitation. However, it should be considered that the sequence of precipitation depends on the solubility of the solid sulfide [10, 11]. An understanding of the distribution of dissolved species in AVS is important to comprehend the biogeochemistry of sulfidic natural systems. In the next step of this study, AVS analyzes will be carried out.

The biogenic sulfides can also be studied trough isotopic analyses. In nature, sulfur has four stable isotopes (^{32}S, ^{33}S, ^{34}S and ^{36}S) with relative abundances of 95%, 0.75%, 4.2% and 0.017%, respectively. In general, the biogenic sulfides are depleted in ^{34}S. It means that the sulfate with lighter sulfur isotopes are preferably metabolized because of their weaker chemical binding. The isotopic ratio (δ^{34}S) used in concert with physical and chemical parameters can provide useful information about the occurrence and extension of sulfur redox processes, one of the mechanisms responsible by natural recovery [6, 13].

2. MATERIALS AND METHODS

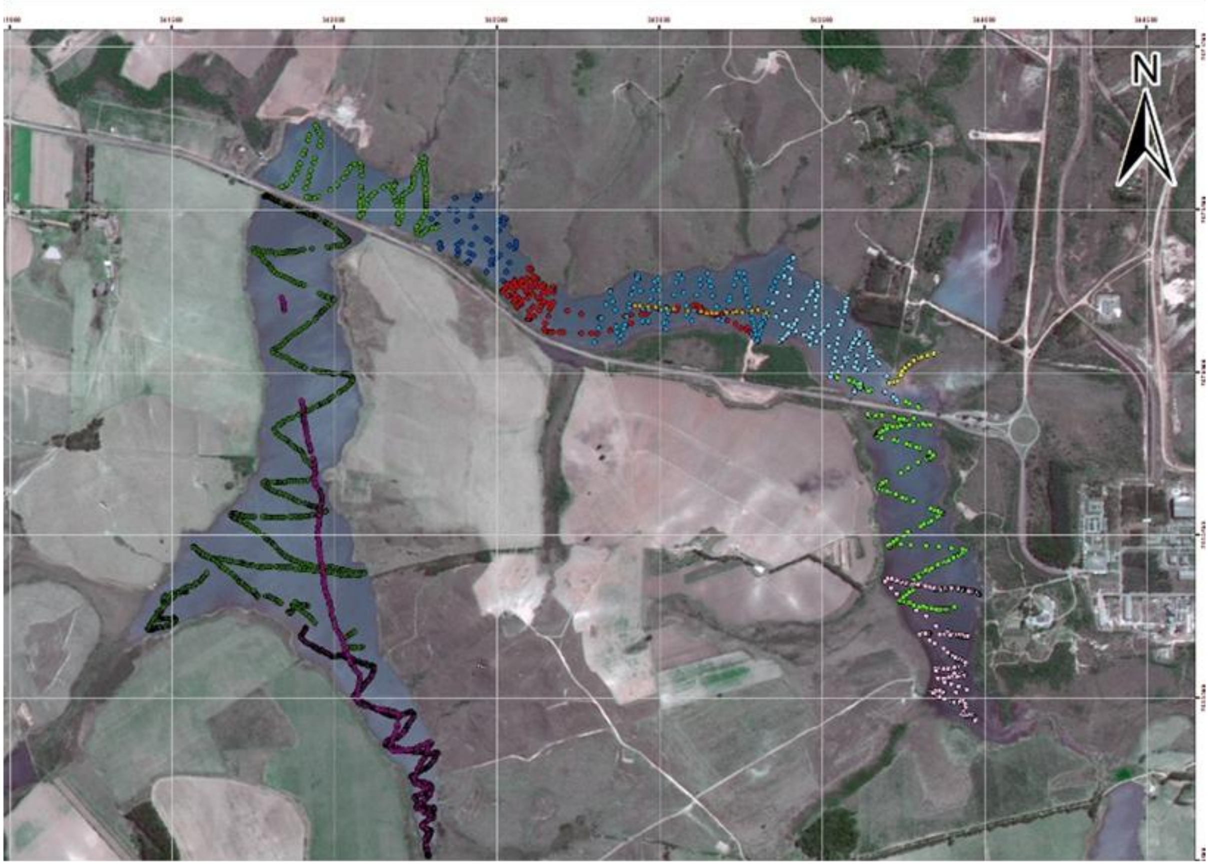
Twenty-six sediment samples were collected in different points including the point of discharge of the treated water and two background points upstream of the water reservoir. For the characterization, the samples were dried, ground, sieved, and then digested in acidic media in microwaves. Uranium and Thorium were determined by spectrophotometry, Ra-226, Ra-228 and Pb-210 by gamma spectrometry and Zn and Mn by ICP-OES.

A bathymetry survey by sonar (GARMIN echoMAP ™ 50dV) in a zig-zag route with a mean distance between the vertices of 100 and 200 meters was performed to determine the thickness of the sediment layer and the data were processed through the Garmim HomePort© software. For regions with water depth less than 50 cm, it was necessary to use a ruler to determine the sediment depth. All the data of characterization and bathymetry were processed using the ArcGIS program.

3. RESULTS AND DISCUSSION

The data of the volumetric survey carried out in the water reservoir are illustrated in the Fig. 1. The data were processed through the ArcGis software. According to the data, the total volume of the reservoir was approximately 3,750,696 m^3 and the sediment volume was approximately 409,848 m^3.

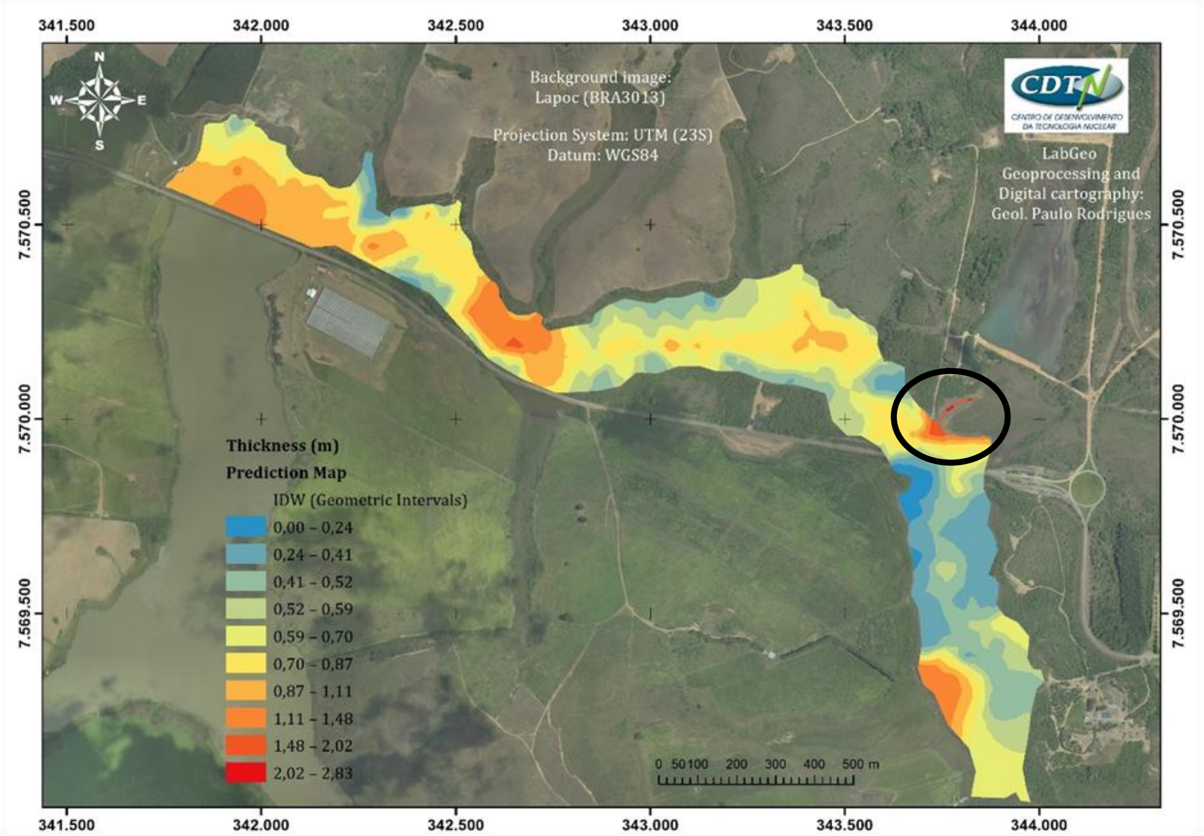
Figure 1: *The Bathymetry Survey Route at the water Reservoir*



Source: Unidade de Tratamento de Minérios - INB

Figure 2 presents the data of the thickness of the sediment layer by interpolation using the settings: IDW (Inverse Distance Weighting) interpolation method and the color classification with 10 classes and geometric intervals. The location of the point, where the treated water is discharged to the reservoir, is highlighted in black in Figure 2. It is observed that the sediment layer in this point is extremely thick, ranging from 1.11 to 2.83 m, similar to the orange region in the left side that is justified by the topography of the region.

Figure 2: *The Sediment Layer Thickness in the water Reservoir*



Source: LabGeo Geoprocessing and Digital cartography: Geol. Paulo Rodrigues - CDTN

According to the sediment volume and the CONAMA Resolution No. 454/2012 [14], twenty – six sampling points were selected in the reservoir. The characterization of all the samples are showed on Table 1.

Table 1: Chemical and Radiochemical Characterization of the Sediments of the water Reservoir.

Elements	**U-nat**	**Ra-226**	**Ra-228**	**Pb-210**	**Th**	**MnO**	**ZnO**
Samples	Bq kg^{-1}	Bq kg^{-1}	Bq kg^{-1}	Bq kg^{-1}	Bq kg^{-1}	%	%
Bkg 013	230	150	< 4100	210	11	0.82	0.06
Bkg 084	160	220	< 4700	280	11	0.45	0.08
0191	6700	880	490	240	490	0.53	0.12
0221	5700	300	370	160	410	0.48	0.12
0231	7700	-	530	430	890	0.08	0.04
0751	7300	-	460	170	520	0.11	0.06
0761	8100	-	460	170	540	0.07	0.03
0971	8400	400	320	140	350	0.64	0.36
0981	5700	150	250	78	460	0.13	0.05
0991	6900	-	290	51	380	0.08	0.22
1001	3900	500	220	280	170	0.07	0.13
1011	3700	480	600	240	920	0.16	0.14
1021	11000	-	430	-	510	0.86	0.19
1031	12000	340	450	140	500	0.06	0.25
1061	8500	160	270	< 23	400	0.29	0.16
1071	12000	440	430	940	86	0.07	0.18
1081	5000	380	540	340	590	0.18	0.17
1091	8100	200	290	310	500	1.13	0.10
1101	11000	570	520	460	310	0.26	0.09
1111	20000	120	250	< 64	370	0.06	0.19
1121	29000	130	360	390	550	0.10	0.17

AM1	340	-	17	< 51	< 270	0.09	0.15
AM2	470	-	< 37	< 48	< 300	0.33	0.15
AM3	200	-	< 37	< 52	< 140	0.14	0.20
AM4	310	32	< 14	< 49	< 250	0.17	0.20
AM5	< 220	< 39	< 29	< 42	< 220	0.45	0.32
AM6	20000	280	340	71	520	0.70	0.62
AM7	160	-	< 26	< 30	< 96	0.19	0.11

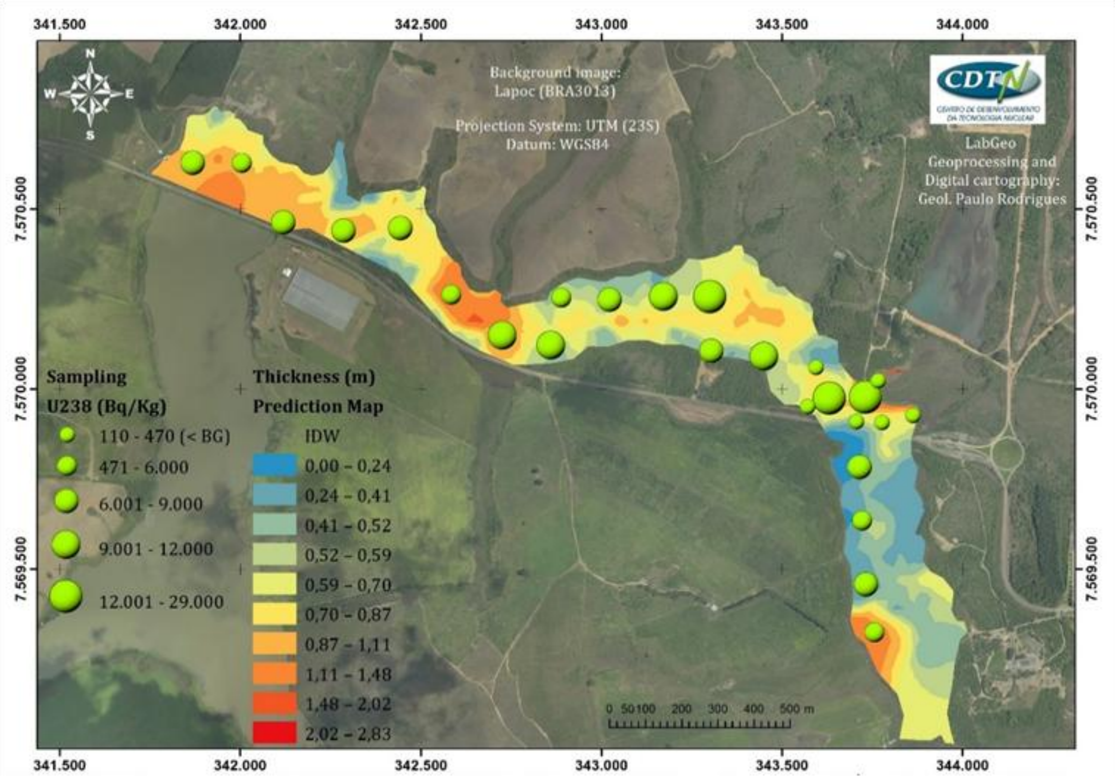
Bkg = background

The two background points, Bkg 013 and Bkg 084, located upstream the reservoir, presented a uranium activity concentration of 230 and 160 Bq kg^{-1}and thorium activity concentration of 11 Bq kg^{-1} in both. The chemical and radiochemical characterization in the sediment samples evidenced a uranium activity concentration ranging from 160 to 29000 Bq kg^{-1} and a thorium activity concentration ranging from 86 to 920 Bq kg^{-1}. All samples presented uranium and thorium activity concentrations higher than the background values, except the U in samples AM3, AM5 and AM7.

Figures 3 and 4 present the activity concentrations of uranium and thorium in the samples, respectively, and its location in the water reservoir. It can be observed that the radionuclides dispersion occurs according to the direction of the water flow in the reservoir. It is important to evaluate in the natural series of U and Th, the radionuclides ^{226}Ra, ^{228}Ra and ^{210}Pb, the ones of most concern from the radiological point of view [15]. It can be seen that sample 0191 presents the highest ^{226}Ra activity concentration (Table 1). This point is located close to the spillway where the waters of the reservoir reach Antas Creek (Ribeirão das Antas), which may be explained by ^{226}Ra high environmental mobility.

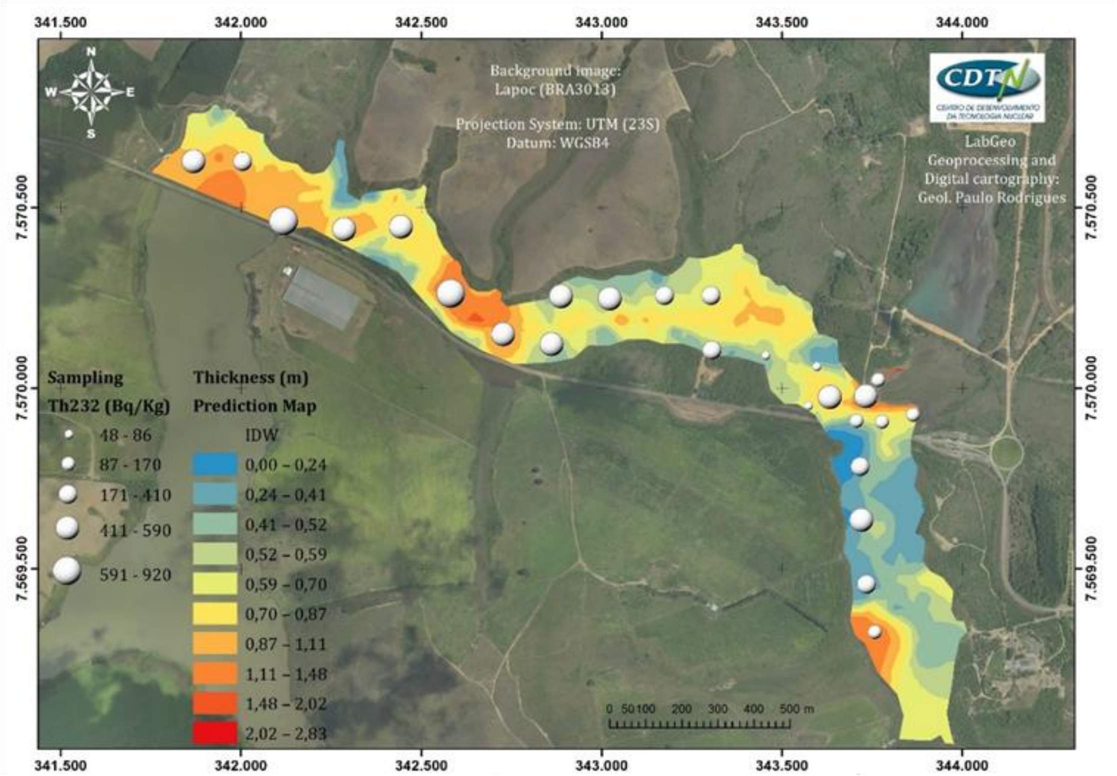
The contents of Mn and Zn range from 0.06 to 1.13 % and 0.03 to 0.62 %, respectively. The two background points presented a Mn concentration of 0.45 and 0.82 % and Zn content of 0.06 and 0.08%.

Figure 3: *Map of the U-nat activity concentration (Bq kg^{-1}) in the water Reservoir*



Source: LabGeo Geoprocessing and Digital cartography: Geol. Paulo Rodrigues – CDTN

Figure 4: *Map of the Th activity concentration (Bq kg^{-1}) in the water Reservoir*



Source: LabGeo Geoprocessing and Digital cartography: Geol. Paulo Rodrigues – CDTN

4. CONCLUSION

The chemical and radiochemical characterization indicated the enrichment of radionuclides and other metals in the sediment samples if compared to the background of the region. However, the evaluation based only on the total concentration of metals is very limited, making it necessary to deepen the studies of mobility and availability of the metal species to the environment. Once the main contaminants were determined, their mobility and migration to the environment as well as the capacity of the system to undergo natural recovery will be assessed.

In some areas, natural recovery may appear to be the most appropriate remedy, mainly for its low cost and for not requiring any type of construction. This option should be considered in the water reservoir, taking into account the key role of sulfide in controlling bioavailability of metals in anoxic sediments as a precipitant agent of toxic metals. In order to assess the potential mobility and bioavailability of the contaminants and to study the role of bacterial sulfate reduction in their immobilization, it is proposed to use the AVS/SEM method along with other speciation tools such as ^{32}S and ^{34}S sulfur isotopic determination.

Other actions may be taken if the rate of sedimentation or the natural recovery are insufficient to reduce contamination within an acceptable period. If this is the case, project managers may consider accelerating the natural recovery process by some engineering mean [7].

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