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PIXE ANALYSES APPLIED TO CHARCTERIZE WATER SAMPLES

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ABSTRACT

Araxá, in Brazil, is a naturally high background area located in the State of Minas Gerais with a population of about 93 672 people. Araxá is historical city famous for its mineral water sources and mud from *Termas de Araxá* spa, which have been used for therapeutic, and recreation purposes. Other important aspect of economy of the city are mining and metallurgic industries. In the Araxá area is located the largest deposit of pyrochlore, a niobium mineral, and also a deposit of apatite, a phosphate mineral both containing Th and U associated to crystal lattice. The minerals are obtained from open pit mines, the minerals are processed in industrial also located in city of Araxá, these plants process the pyrochlore and apatite to obtain the Fe-Nb alloy and the concentrate of phosphate, respectively. Studies were developed in this area to assessment the occupational risk of the workers due to exposure to dust particles during the routine working, however very few studies evaluated the water contamination outside the mines in order to determine the metal (stables elements) concentrations in water and also the concentrations of the radionuclides in water. This paper presents the previous results of a study to identify and determine the concentrations of metals (stables elements) and radionuclides in river around the city. The water from these rivers is used as drinking water and irrigation water. The water samples were collected in different rivers around the Araxá city and the samples were analyzed using PIXE technique. A proton beam of 2 MeV obtained from the van de Graaff electrostatic accelerator was used to induce the characteristic X-rays. S, K, Ca, Cr, Mn, Fe, Ni, Zn, Ba, Pb and U were identified in the mass spectrum of the samples. The elemental mass concentrations were compared using a non-parametric statistical test. The results of the statistical test showed that the elemental mass concentrations did not present the same distribution. These results indicated that there was more than one source for the elements, environmental and anthropic sources

1. INTRODUCTION

Water is essential to life on our planet. A prerequisite of sustainable development must be to ensure uncontaminated streams, rivers, lakes and oceans. In addition to the urban pollution the mining and milling processes are the mains source of water contamination. In this context, waters resources have been increasingly penalized with several launches of waste resulting from population growth and disorderly occupation of protected areas [1].

The main sources of human exposure to natural radiation are the radionuclides present in the earth surface: the radionuclides from natural series from ^{238}U and ^{232}Th (53%), ^{40}K (17%) and cosmic rays. However, it should be highlighted that in addition to external exposure, humans are also exposed to internal contamination due to ingestion of food and drinking water and inhalation of radioactive particles, as radon. [2-3]

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Studies were developed in this area to assess the occupational risk of the workers due to exposure to dust particles during the routine working, however very few studies evaluated the water contamination outside the mines in order to determine the metal (stables elements) concentrations in water and also the concentrations of the radionuclides in water. [3,6, 7].

2. METHODS

Nineteen surface water samples were collected during September 2009 and they were transported in plastic bottles to the Aerosol Characterization laboratory at IRD. In this preliminary study the pH of each sample was determined *in situ* and after the pH measurement, a drop of pure nitric acid was added to each sample to reduce the ion attachment in the internal wall of the plastic bottles. At the laboratory, the samples were transferred to glass beakers capped with watch glasses and they were evaporated at low temperature (<50 ºC). The beaker walls and the watch glasses were washed using Milli-Q water and the volume of each sample was reduced to 10 mL. The possible contamination of the water samples was evaluated using a sample of Milli-Q water was evaporated using the same experimental arrangement of the samples. A drop of 2 μL was dropped on a Mylar film and dried at room temperature, and they were analyzed using PIXE (Particle Induced X-ray Emission) technique. **[**8,9,10**]**

PIXE technique is a non-destructive technique with a low detection limit that allows to identify and to determine the mass concentration of the elements heavier than Na (Z=11) and since 1970 it has been employed for analysis of environmental samples. The absolute efficiency was determined for the elements heavier than Na. This curve was tested using Fe and U standard targets before beginning the irradiation of each set of samples. The error associated to the analytical technique is 1.2 % [11,12].

3. RESULTS

The pH values of the water were between 5.5 and 7.0. The average concentrations of the metals in the 19 surface water samples collected in Araxá are shown in Figure 1. S, K, Ca, Cr, Mn, Fe, Ni, Zn, Ba, Pb and U were identified in the mass spectrum of the samples.

The results indicate that the water contained elements from anthropic sources and also from natural sources. Elements as S, Co, Ba and U identified in the water surface samples could be from natural or anthropic sources.

The elemental mass concentrations were compared using a non-parametric statistical test (Mann-Whitney rank and α=0.05). The results of the statistical test showed that the elemental mass concentrations did not present the same distributions. These results indicated that there was more than one source for the elements, environmental and anthropic sources.

The concentrations of metals in water were compared to the values recommended by the USEPA (United State Environmental Protection Agency) for metals concentrations in water. The concentrations of metals in the samples water collected in this preliminary study were below the limits recommended by USEPA, except the uranium concentrations. [13]

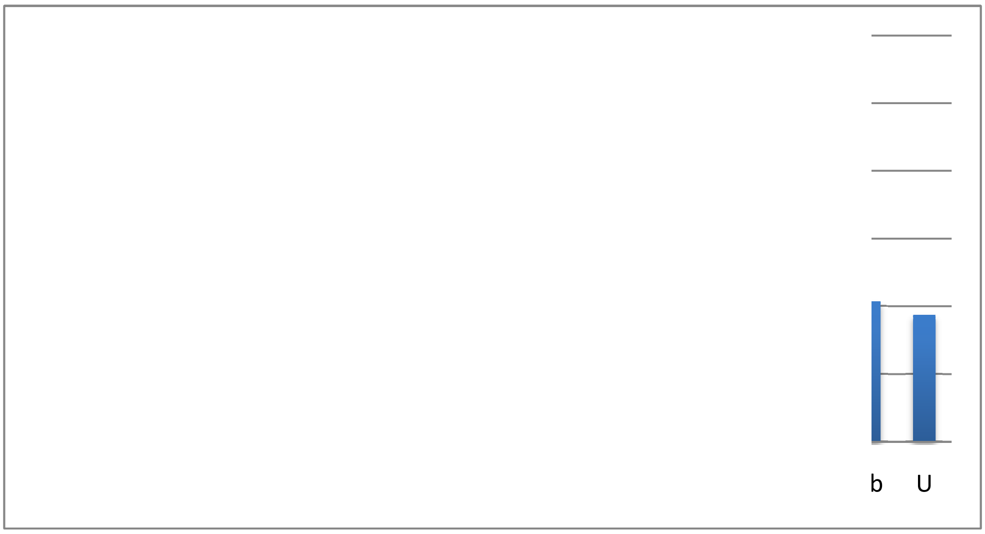

Figure 1 Average concentrations of elements identified in the surface water samples collected in Araxá

Araxá is located in mineralogical region and it is famous for its mineral water, including the radioactive water containing Rn. This geological characteristic could justify the identification of the metals in surface water. But should not be excluded the possibility of an anthropic contamination. In addition, in Araxá is located the largest pyrochlore deposit in world. Pyrochlore is Nb mineral containing Th and U associated to the crystal lattice and it is processed to obtain the Fe-Nb alloy. The industrial process used to produce the Fe-Nb alloy is complex involving different steps and also different chemical substances. The slag produced during the process is deposited in dumps, technically prepared for it. Although the slag produced during the metallurgic processing is insoluble, the weathering can dissolve the metals compounds present in slag and these metals can leak to the environment. The concentration of these metals leached by weathering process usually is very low, however they can migrate in soil and can contaminate the underground water.
The U concentrations in water samples were compared to limit adopted by USEPA for U concentration in drinking water. The U concentrations in 4 surface water samples were above the USEPA limit (30 μg/L). The uranium concentration in each water sample is shown in Figure 2.

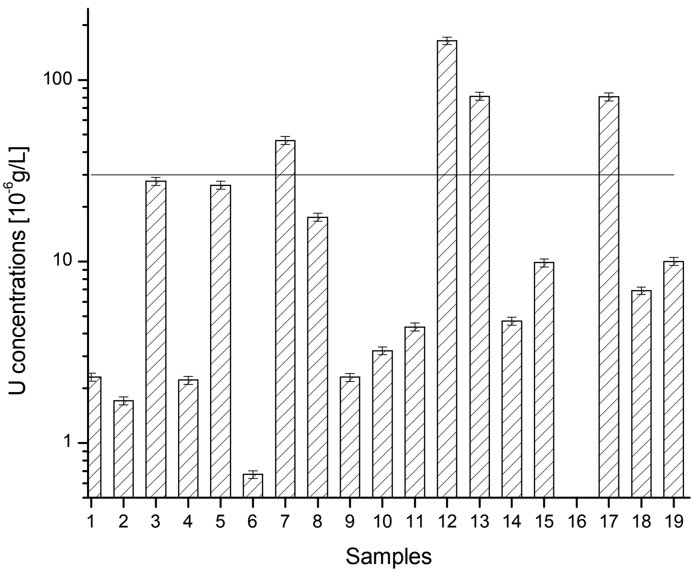

Figure 2 Uranium concentrations in 19 surface water samples collected in Araxá and the USEPA uranium limit.

The presence of these metals in surface water could be caused by natural process, as leaching of water in soil and rock, or caused by anthropic sources as contaminating of the underground water by leaking in industrial dumps, leaching of minerals or trail piles.

However, independently the source of the metal, the inhabitants of Araxá could be exposed to toxic metals, and based on these results, we recommend a detailed study to evaluate the risk for the inhabitants and to identify the source of metals present in the surface water.

3. CONCLUSIONS

Although the concentrations of metals (stables) in the water samples were below the limits recommended by USEPA it was identified toxic elements as to toxic metals (stables) as Cr, Co, Ni, Ba and Pb in the water. However the uranium concentrations in 6 surface water samples are above limit for drinking water adopted by the USEPA (30 µg/L). The results of this preliminary study indicate that the population of Araxá could be exposed to toxic metals and we recommend a detailed study to identify the possible metal sources.

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