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Concentrations and History of Heavy Metals in Sediment Cores: Geochemistry and Geochronology Using ^{210}Pb

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***Abstract*—**This paper aims at assessing the concentrations of heavy metals and the isotopic composition of lead ^{210}Pb in different fractions of sediment produced in the watershed that makes up the Mãe d'água dam and thus characterizing the distribution of metals along the sedimentary column and inferencing in the urbanization of the same process. Sample collection was carried out in June 2014; eight sediment cores were sampled in the lake of the dam. For extraction of the sediments core, a core sampler "Piston Core" was used. The trace metal concentrations were determined by conventional atomic absorption spectrophotometric methods. The samples were subjected to radiochemical analysis of ^{210}Po. ^{210}Pb activity was obtained by measuring ^{210}Po activity. The chronology was calculated using the constant rate of supply (CRS). ^{210}Pb is used to estimate the sedimentation rate.

***Keywords*—**^{210}Pb dating method, heavy metal, lakes urban, pollution history.

I. Introduction

THE knowledge about sediment transportation is very important, because the sediment transport through leaching generates the sedimentation of the reservoirs, and cause problems such as urban flooding and environmental degradation. Understanding the dynamics of sediments of a water basin has great importance, for example, changing land use and occupation, urbanization or economic development and affecting climate changes.

The sediments are found in layers in the form of finely divided particles at the bottom of rivers, lakes, reservoirs, bays, estuaries and oceans. These consist, generally, of various minerals with fine, medium and thick grain, including clays, silt and sand mixed with organic matter, and its composition (mineral and organic) depends on geology and local biota, while the size of the particles varies according with of its origin conditions [1].

Sediment accumulated in estuaries and lakes is a valuable historical record of contamination processes by anthropogenic source. The geochronology of sediments, acts as an implement in determining the recent history of it.

In the urbanized environment, the occurrence of trace elements is more likely between aggregate of sediments, generated in a natural or anthropogenic way. The metals can be associated with contamination, but we must be cautious in analyzing metal concentration presented in the sediment, since they are crucial for decision-making and essential to both plants and animals.

According to [2], several studies of heavy metals in ecosystems showed that large areas near urban complexes, such as metal works and highways have high concentrations of these elements. The accumulated metals in soils are slowly exhausted through processes of absorption by plants, leaching or erosion [3].

The process of sedimentation in aquatic environments and its relationship with anthropic effects have great importance for the understanding of geochemical processes of releasing metals in urbanized areas.

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II. Materials and Methods

A. Sampling

Sampling area is Mãe d'Água dam and it is located in the Porto Alegre city, Rio Grande do Sul state, southern Brazil. The Mãe d'Água dam is a tributary to the Arroio Dilúvio, important watercourse which runs through the Porto Alegre city, cutting it eastbound.

The Mãe d`Água dam is the outlet of four streams, corresponding with an area of 353 hectares, and is located on the Campus do Vale of the Federal University of Rio Grande do Sul. Fig. 1 shows the study area, featuring the location and size of the dam.

B. Urban Sediment Sampling

The sampling was carried out on 6/9/2014. The collection points of the sediment cores were planned pursuing a better spatial distribution in the lake and respecting the place's hydrodynamics. Four points were chosen to represent the study area [9].

The sediments core were sampled and their data were tabulated as the geographical coordinates of points, the water height and the length of the sediments profile according to Table I.

Core sampler was used to sample. Introduced a cylindrical tube of hard PVC (75 mm diameter) into the bottom sediment is in this method.

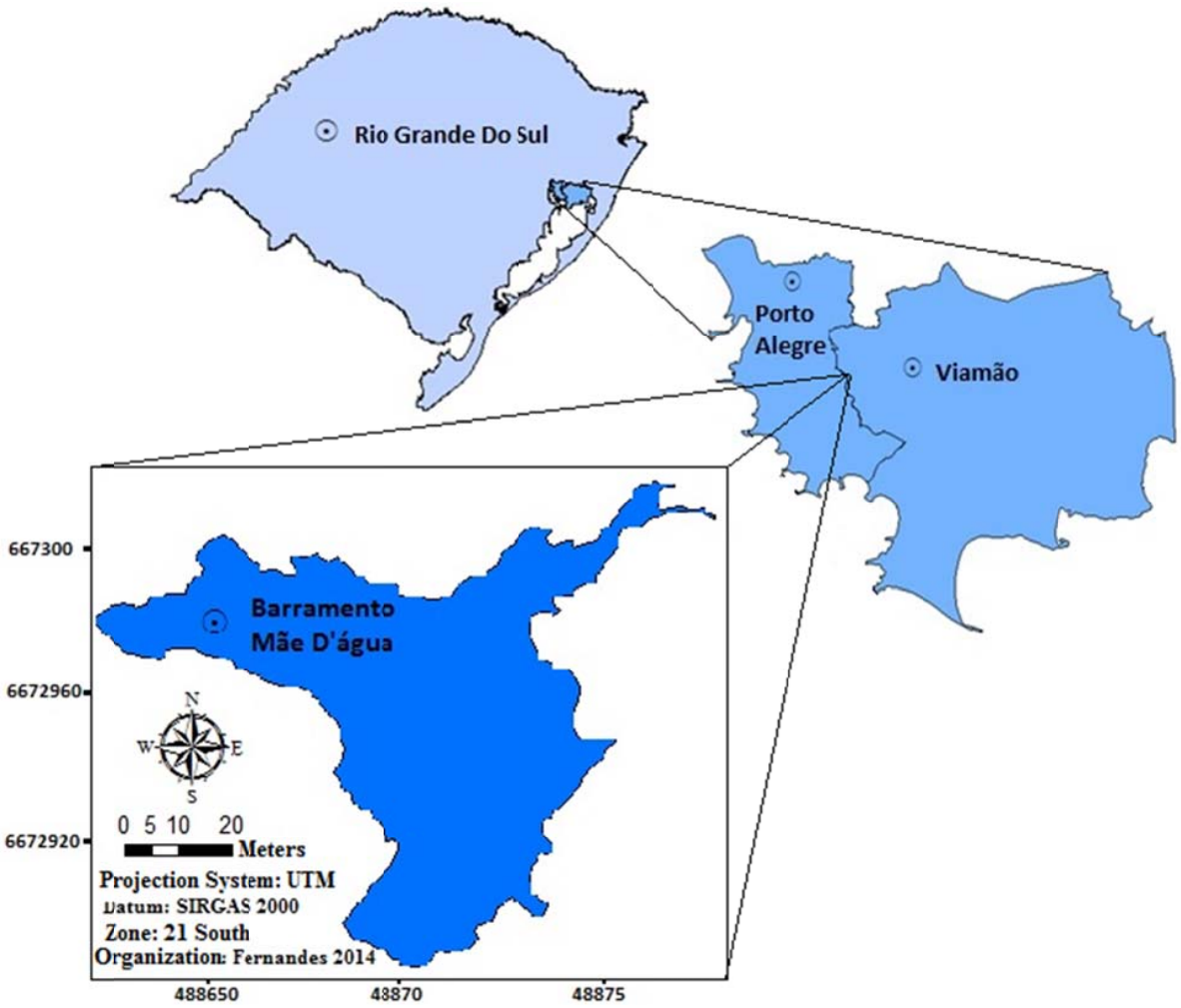

Fig. 1 Location and representation of the study dam in the Metropolitan Area of Porto Alegre- RS

TABLE I
INFORMATION OF THE COLLECTED SEDIMENT CORES

Sample (Core Sampling)	UTM coordinates (m) (Ellipsoid WGS-84)		Water line (m)	Core sampling length (m)
	X	Y		
T1	488716,34	6672912,68	0,40	0,52
T4	488729,65	6672984,72	0,40	0,52
T6	488681,47	6672977,90	0,40	0,52
T8	488633,55	6672976,31	0,40	0,52

C. Laboratory Analysis

Sediments for metals and 210Pb analysis were digested in a mixture of 5:4:1 HNO3+HCl+HF using a microwave system (CEM MDS 2000).

Metals were analyzed by Atomic Absorption Spectrometry (Ni and Zn by flame).

Analytical quality control was made with reference material from USGS laboratory. It was carried out to ensure the quality control of the analyses (Table II). The recovery levels determined in this study showed good reproducibility, demonstrating that the methodology shows good development of the detection of digestion of metals (Zn and Ni) in study.

Total 210Pb (210Pbtot) was determined by alpha spectrometry through its granddaughter 210Po, assuming secular equilibrium. 210Po and 209Po (yield tracer) were spontaneously deposited onto a silver disc [5] which was counted on a standard silicon surface barrier detector.

TABLE II
CONCENTRATIONS OF ZN AND NI IN THE REFERENCE MATERIALS, GREEN RIVER SHALE (SGR-1B) AND CODY SHALE (SCO-1), OF THE USGS[A]

Element	Certified sample	Determined in this study by ICP-OES
	Mean ± SD	Mean
	Green River Shale (SGR-1b)	
Ni (mg.kg^{-1})	29± 5	27
Zn (mg.kg^{-1})	74 ± 9	77
	Cody Shale (SCo-1)	
Ni (mg.kg^{-1})	27 ± 4	24
Zn (mg.kg^{-1})	103 ± 8	110

[a] United States Geological Survey; SD = Standard Deviation.

III. Results and Discussion

A. Total Zinc Concentrations in Sediment Cores

In the urban areas, dust particles arranged in traffic routes come into contact with the waste of wear and vehicle emissions, which is one important source of metal-trace [6], [8], especially Zn^{2+}.

Fig. 2 shows the vertical distribution of the levels of zinc (in ppm) in different sediment cores (T1, T4, T6 and T8, respectively) of sediment deposited as the bottom of the Mãe d'água dam. Sediment samples have showed values above local background values (47,4 mg.kg^{-1}), and the anthropic activities within the water basin explain the increase in the concentration of Zn Excepting the core T4, which shows a reduction in certain values, all profiles showed an enrichment of Zn along the sedimentary deposition process. According to [2], Zn is a quite remarkable element, present in relatively high amount when compared to other metals, such as copper (Cu), lead (Pb) and nickel (Ni).

The sediment core T1 in the first layers near the surface showed as the most polluted, with 597 mg.kg^{-1}, on the other hand the sediment core T6 showed the lowest concentration in the extract in the base (25 mg.kg^{-1}). On the average data analysis, the core T6 also appears as the point of deposition that the sediments show less association with metal-trace Zn and core T8, the largest. The results in core T1 show concentration values on the surface that lead to an increase of the average value.

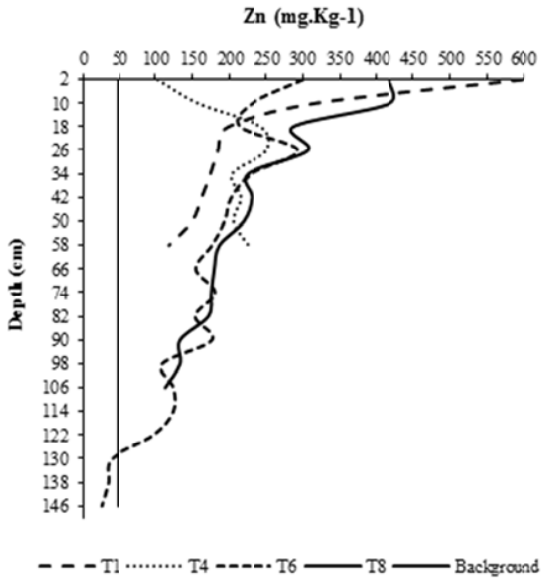

Fig. 2 Distribution of zinc content in depth, in sediment cores in Mãe d'água dam

B. Total Nickel Concentrations in Sediment Cores

The levels of nickel (Ni) in sediment cores from the bottom of the Mãe d'água dam are shown in Fig. 3. It shows that nickel concentrations were bigger than local background (4, 9 mg.kg^{-1}). This result is probably due to the urbanization of the study area. It happened because anthropogenic processes as building, industrialization and residues discharge (liquid, solid and gaseous) have high concentrations of metals.

The sediment core 1 in the first layers near the surface are as the most polluted, with 17 mg.kg^{-1}, on the other hand the sediment core 4, showed the lowest concentration in the extract in the base (12 mg.kg^{-1}). In the average data analysis, the T6 also appears as the point of deposition where the sediments show less association with metal-trace whereas the behavior of the testimonies, T1, T4 and T8, are the largest.

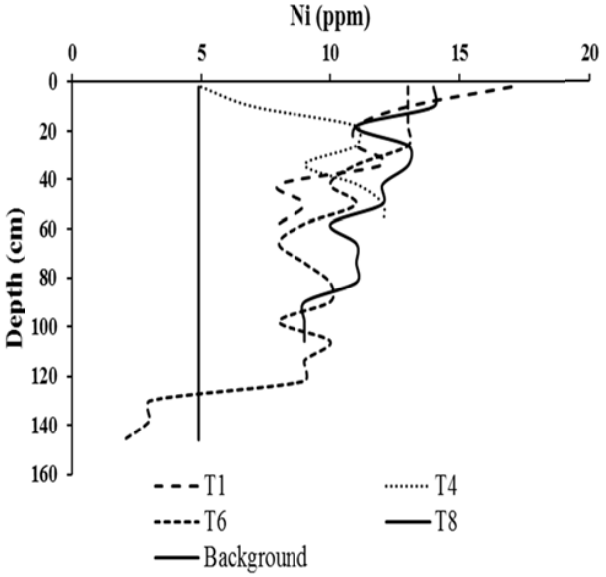

Fig. 3 Distribution of nickel content (ppm) in depth, in sediment cores in Mãe d'água dam

IV. Conclusion

Zn and Ni elements showed elevated concentrations in recent sediment fractions. On the surface of the sediment cores, T1, T6 and T8 are the largest concentrations of these metals, demonstrating the existence of the enrichment of sediments by these elements, and that all strata of sedimentary column analyzed showed concentrations above background values. This linked is evidenced to the urbanization of the area, and anthropogenic processes favoring the gradual growth of concentrations towards the surface, represent the most recent deposition.

This kind of study must be accompanied with analyses of temporal and spatial variability of concentrations of metals in sediment samples, as it has been carried out, in order to suggest new useful alternatives in management of sediments, with the aim of reducing the risks that these contaminants can represent to the health of population and to watershed ecosystem.

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