

## U, TH AND LANTHANIDES IN STREETSOILS OF SÃO PAULO CITY, BRAZIL

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### ABSTRACT

The study of lanthanide distribution in urban environments has become of interest over the last years, due to the increased industrial use of these elements. São Paulo is the 6<sup>th</sup> largest metropolitan region of the world, with about 20 million inhabitants in its metropolitan area, more than 9 million motor vehicles and intense industrial activity. There is little information on U, Th, and lanthanide contents in urban soils, and there are as of yet no reference values for these elements in soils of São Paulo city. The present study aimed to determine U, Th and lanthanide concentrations in soils adjacent to avenues of highly dense traffic downtown in São Paulo city, to assess their possible sources and potential environmental impacts. The analytical technique employed was Instrumental Neutron Activation Analysis (INAA). Th and U levels ranged from 4.0 to 37.0 mg kg<sup>-1</sup> and from 1.6 to 18.7 mg kg<sup>-1</sup>, respectively. These values are higher than literature values for U and Th in Brazilian superficial soils. The results obtained for the lanthanides indicate enrichment in La and Ce. However, a possible anthropogenic source should be investigated since high background values of these elements may be associated to the natural geological composition of the soils.

### 1. INTRODUCTION

Lanthanides are being used more and more in technological industrial production, and this can affect the concentration level of lanthanides in urban environments. Some of the applications of mixed rare earths are as metallurgical additives for ferrous and non-ferrous metals, fluid cracking catalysts, lighter flints, polishing compounds in glasses, carbon arc cores for lighting and hydrogen absorbing alloys for rechargeable batteries. Some of the salient applications of high-purity rare earth elements are cathode ray tubes, permanent magnets in computer technology and sound systems, lasers, phosphors, electric motors, optical fibers, and possible future applications such as in colored pigments for plastics and paints, new catalysts, refrigeration systems and solid oxide fuel cells [1]. Furthermore, Ce, La and Nd are being used in automobile catalytic converters to minimize toxic gas emissions. However, abrasion and deterioration of this vehicle component release small amounts of these elements to the environment. This can cause lanthanide deposits in vegetation near major roads and highways as well as other environmental compartments, like soils [2]. On the other hand, agricultural uses of phosphate fertilizers may increase lanthanide and uranium concentrations in the environment. The production and use of phosphate fertilizers may cause Rare Earth Elements (REE) emissions both to the atmosphere and to the soil. Uranium presence in fertilizers is a consequence of the natural occurrence of this element in phosphate rocks usually employed as a source of phosphorous in phosphate fertilizer production [3-5].

Studies performed by de Souza & Ferreira [6] in samples of fertilizers highly commercialized in the State of São Paulo showed a range of concentration of 7.93 to 21.83 mg.kg<sup>-1</sup> of natural Uranium and 47.1 to 153.0 mg.kg<sup>-1</sup> of natural Thorium. The use of REE in agriculture has been observed as a potential environmental problem in China [7].

The use of phosphogypsum, which originate primarily from the source phosphate rock used in fertilizer production, and that has been used in building materials, may also increase the uranium levels in the urban soils.

Urban soils show great variability in their composition and characteristics, not only for natural parameters such as pH or cation exchange capacity, but also for pollutants. In a city environment, this variability is directly affected by human activities that influence soil composition, such as excavation, redistribution, soil matrix mixing and addition of extraneous materials due to building construction and different uses of urban land. These together can modify soil properties in an unpredictable manner [8].

With about 20 million inhabitants, São Paulo is the biggest city in South America, and presents many pollution related problems. There are few data on U, Th and lanthanide concentrations in Brazilian soils and almost nothing in São Paulo urban soils. In previous studies, U, Th and rare earths levels were determined in urban park soils of São Paulo city [9,10]. In the present paper, which is part of a main project that assesses metals in urban soils of São Paulo city [11], U, Th and lanthanide distribution and ratios were determined in streetsoils of São Paulo city. The results were compared to literature data and their possible sources were evaluated.

## **2. MATERIALS AND METHODS**

### **2.1. Sampling**

Seven important avenues of São Paulo city with high density traffic altering between constant speed and stop-and-go traffic were selected. Two of the main arteries run along the two main rivers that cut across the city (Pinheiros and Tietê rivers) and are considered to be the most congested of South America, with about 400,000 vehicles/day [12].

The distance between the sampling points was from 3 to 5 km, providing 110 samples in 36 points all over the city's metropolitan region. Areas of 1m<sup>2</sup>, forming a rectangular grid, were sampled. The sampling took place from the grass strip 15 cm next to the asphalt up to 115 cm from the roadway. Composite samples were prepared, from 3 samples, collected at each point of the rectangle. The sampling depth was from 0 to 5 cm. A polyethylene tube with 4 cm diameter was used to collect the samples, which were placed in air-tight polythene bags, labeled, and brought to the laboratory for analysis.

### **2.2 Analytical Procedure**

Once in the laboratory, samples were dried at 40°C and sieved through plastic-only sieves into fractions lower than 2 mm – before and after sieving, the samples were homogenized, quartered and grinded in an agate mortar.

For the analysis process, approximately 100 mg of each sample was placed in a pre-cleaned inert plastic bag and weighted; samples were then placed inside an aluminum vessel, together with the standard reference materials Soil 7 (IAEA), GS-N and BE-N (GIT-IWG), and irradiated for 8 hours at a thermal neutron flux of  $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$  in the IEA-R1 nuclear reactor. The reference materials GS-N and BE-N were used as standards (literature values), in the comparative INAA method. The samples were then counted twice using an HPGe detector; the first counting series was performed after 7 days of the irradiation and the second one 15 days after irradiation; the counting times varied from 1 to 2 hours, and gamma-ray spectra were analyzed using the VISPECT software in order to obtain the gamma peak areas. The quality of the determinations was assessed by the analysis of the certified reference materials Soil-7 (IAEA). The results showed good accuracy (relative errors to certified values < 5% for most of elements) and acceptable precision (relative standard deviations < 15%).

### 3. RESULTS AND DISCUSSION

The results obtained for U and Th concentration levels, as well as concentrations data reported in other studies, are presented in Table 1. It can be seen that, in relation to Brazilian superficial soils [13], streetsoils of São Paulo presented higher concentrations for U and similar levels for Th. On the other hand, in relation to international data, this work presented higher levels for U and Th, except for U in the study of Yamaguchi et al. [4], which studied soils after long-term application of phosphate fertilizers. In relation to urban park soils of São Paulo [9], uranium presented higher concentrations and thorium showed similar concentrations.

**Table1. Uranium and Thorium range concentrations ( $\text{mg kg}^{-1}$ ) in São Paulo streetsoils compared with data reported in the literature**

<b>Avenue</b>	<b>URANIUM</b>	<b>THORIUM</b>
Marginal Tietê	1.6-5.1	11-27
Rebouças	3-5	8.7-31
Radial Leste	2.6-5.3	10-22
Jacu Pêssego	2.2-15	10-37
Marginal Pinheiros	2.4-19	4-36
23 de Maio	3.1-3.4	16-17
<b>Other studies</b>		
Perez <i>et al.</i> [13]	0.001 – 2.11	0.003 – 38.08
Kucera <i>et al.</i> [14]	1.8 – 3.20	8.0 – 15.50
Yamaguchi <i>et al.</i> [4]	0.08 – 14.00	-
Sterckerman <i>et al.</i> [15]	2.45 – 2.33	9.40 – 10.30
Camargo et al. [9]	1.9 - 8.6	8.4 – 38.0

The results obtained for U and Th levels may be associated to the natural geological composition of the soils, since sedimentary rocks of the Tertiary Basin of São Paulo are the main parent material of São Paulo soils. Nevertheless, the influence of the use of phosphogypsum in building material in uranium concentrations may not be discarded.

The results obtained for the lanthanide concentrations, as well as Earth' crust levels, reference data for unpolluted soils levels, provided by the National Institute of Public Health and the Environment – RIVM from the Netherlands [16], and from São Paulo park soils [10], are presented in Table 2. The concentration levels were similar to those obtained in urban park soils of São Paulo. The lanthanides presented concentration levels higher than the guiding values of the RIVM. For Ce, RIVM has established 53 mg kg<sup>-1</sup> as the maximum permissible concentrations, and the results obtained were much higher than this value [16].

The normalization of REE concentrations with respect to a geological “reference” value is a useful tool to obtain a comparison among information from “contamination” sources [18]. The results obtained and the earth's crust levels were normalized in relation to chondrite values as reference values (Fig. 1). An enrichment of the light REE (La to Sm), in contrast to the heavy REE (Eu to Lu), was observed, just as in the earth's crust. A negative anomaly of europium was observed. Europium can have a divalent state, and due to this characteristic, it can show a different behavior from the other REE. In the divalent state it can be strongly incorporated to feldspats (and plagioclase), and when this mineral is withdrawn by fractionated crystallization, Eu concentration decreases in relation to the neighbors Sm e Gd (or Tb), giving rise to negative anomalies of Eu in the parent material. The lanthanides pattern is related to the sedimentary rocks of the Tertiary Basin of São Paulo, which are the main parent material of São Paulo soils. Therefore, the enrichment in light REE can not be attributed to anthropogenic origin, due to the high background values associated to the natural geological composition of the soils.

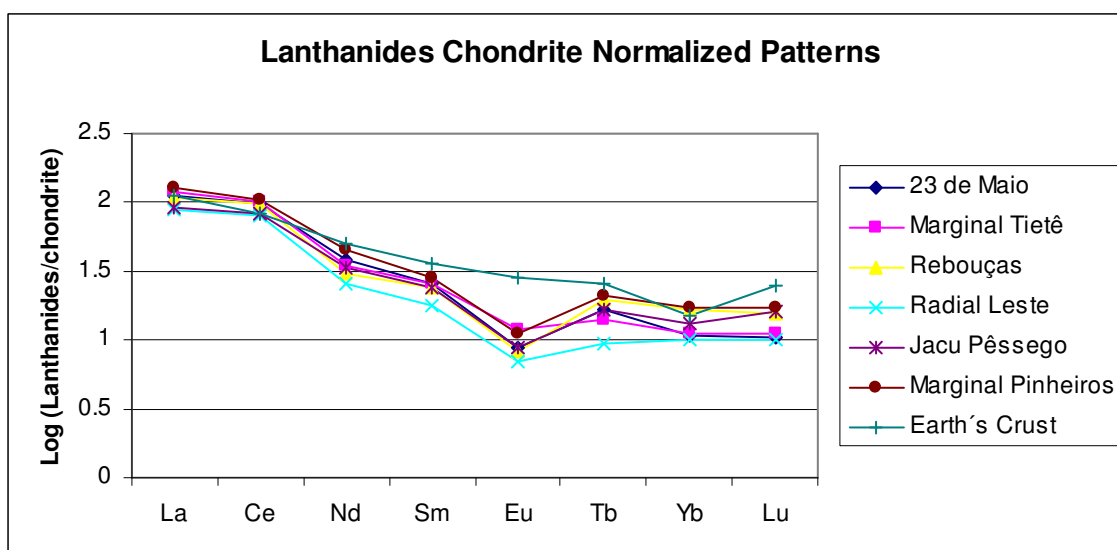


Fig. 1 Lanthanides chondrite normalized patterns

### **3. CONCLUSIONS**

The results obtained for U, Th and lanthanides in streetsoils of São Paulo showed higher concentrations than reference and literature values. Due to the high background values associated to the parent material, though, these results may not indicate anthropogenic sources. Nevertheless, the increasing use of lanthanides in technological industries, as well as the presence of U and lanthanides in fertilizers, and of U in building materials, requires continuous environmental monitoring.

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**Table 2. Means and range concentrations of rare earth elements in streetsoils of São Paulo and literature values (mg kg<sup>-1</sup>)**

Avenues	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
<b>Marginal Tietê</b>	36.5 20-63	81.0 52-123	28.1 14-47	5.0 2.4-8.5	0.88 0.63-1.4	0.67 0.48-1.3	2.3 1.1-4.5	0.36 0.22-0.56
<b>Rebouças</b>	34.1 21-49	78.7 53-122	24.5 14-41	4.7 4.2-7.6	0.61 0.46-0.76	0.92 0.27-1.2	3.4 0.96-7.0	0.50 0.16 - 0.94
<b>Radial Leste</b>	27.1 15-33	67.9 32-98	20.3 11-29	3.5 2.2-4.0	0.52 0.37-0.63	0.44 0.30-0.61	2.06 0.28-3.1	0.32 0.23-0.43
<b>Jacu Pêssego</b>	27.9 20-88	66.1 38-196	27.1 13-107	4.7 2.8-17.4	0.64 0.43-1.4	0.79 0.35-1.8	2.7 1.5-4.1	0.51 0.30-0.67
<b>Marginal Pinheiros</b>	39.5 15-77	83.3 36-186	36.0 20-70	5.6 3.0-11.3	0.81 0.41-1.6	0.96 0.71-1.24	3.6 2.4-4.8	0.56 0.40-0.65
<b>23 de Maio</b>	34.8 21-49	79.5 53-106	30.5 18-43	5.0 2.8-7.2	0.65 0.54-0.76	0.68 0.59-0.76	2.3 1.7-2.8	0.33 0.25-0.42
<b>Soil concentration unpolluted soil [16]</b>	40	-	40	7	2.3	1	3	0.7
<b>Urban park soils of São Paulo [10]</b>	8.4-82	24-222	2.5-75	1.07-13.4	0.06-2.72	0.02-2.04	0.79-9.0	0.13-1.00
<b>Earth's crust (means)[17]</b>	35	66	40	7.0	2.1	1.2	3.1	0.8

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