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Rare earth elements, U and Th in tunnel dusts of São Paulo city, Brazil

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ABSTRACT

São Paulo is one of the most populated cities in the world, with about 20 million inhabitants in its metropolitan area, more than 12 million motor vehicles and intense industrial activity. Given its importance as a major urban center in South America and the lack of information concerning urban dust composition, the present study aimed to determine rare earth elements (REEs), U and Th mass fractions in tunnel dust, collected in the Jânio Quadros Tunnel, and to assess their possible sources. The study of REEs distribution in urban environments has become of interest over the last decades, due to the increasing industrial use of these elements. The REEs, that are as common as the most familiar metals, are found in metallurgical additives, fluid cracking catalysts and automobile converter catalysts, among other applications. In this study, which employed Instrumental Neutron Activation Analysis (INAA) as analytical technique, the mass fractions of eight REEs were determined and normalized to the chondrite concentration values. The results showed that major concentrations were found for light REEs, following the sequence Ce > La > Nd > Sm > Yb > Eu > Tb > Lu. The pattern of the results pointed to a natural origin for these elements. Regarding U and Th concentrations, the results varied between 1.0 – 9.4 μg g^{-1} and 3.3 – 35.9 μg g^{-1}, respectively. Since there is almost no information about the concentration of these elements in this kind of matrix in São Paulo city, these data are important to support further investigations.

Keywords: Tunnel dusts, rare earth elements, INAA.

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1. INTRODUCTION

Rare Earth Elements (REEs) are a group of metals comprised by the fourteen lanthanide elements, plus yttrium and scandium. They have similar physicochemical properties and are often found together in the same ores and deposits. Despite of the name "rare", some of them are as common as the most familiar metals in the composition of the Earth's crust. They are commonly divided into two categories: the light REEs (LREEs), which include lanthanum, cerium, praseodymium, neodymium, samarium, europium; and the heavy REEs (HREEs), formed by gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, scandium and yttrium.

In the last decades, the use of REEs in industrial activities rapidly increased, and, nowadays, these elements are found in several industrial products, such as metallurgical additives, fluid cracking catalysts and automobile converter catalysts, polishing compounds in glasses, rechargeable batteries, electronic components in cell phones and flat panel displays, and magnets, among other applications. One of the most important uses of REEs, as above mentioned, is their application to automobile converter catalysts, in which these elements (mainly Ce, La and Nd) help to achieve high levels of conversion of CO, HC and NO_x into harmless compounds, such as CO_2, H_2O and N_2. The main components of these catalysts are precious metals (more commonly Pt, Pd and Rh), and inorganic oxides, such as CeO_2 and ceria-based composite oxides [1-2].

Regarding this type of application, it is well know that abrasion of automobile catalysts can release metals into the environment, including Pt, Pd, Rh and REEs. This is important because of two factors: the decline of catalytic activity of damaged catalysts, and the consequent release of harmful components into the environment; and the possible consequences of the accumulation of released REEs and other metals, including those concerning human health. Although the associations between the intake of REEs and its consequences to human health are yet a less explored issue and, at the same time, controversial, there is some research pointing to a negative role of some REEs (mainly Ce, La and Gd) in the development or aggravation of some lung, kidney, liver and brain conditions [3-4]. These aspects are of major importance, considering the continuous increase of the automobile fleet, mainly in urban centers and megalopolis, like São Paulo City. São Paulo is one of

the most important regions in South America, with about 20 million inhabitants in its metropolitan area, eight million motor vehicles in its fleet [5] and intense industrial activity.

Despite of this importance, there are still few data on REEs, U and Th concentrations in São Paulo urban dusts, and almost none related to tunnel dust. In previous studies, the concentrations of these elements were only determined in urban park soils [6-7] and in urban street soils of the city [8]. Aiming to give a contribution to fulfill this lack of information, in this study, samples of tunnel dusts were analyzed in order to access its composition, focusing on the determination of the mass fractions of REEs, Th and U.

2. MATERIALS AND METHODS

2.1. Sampling

The dust samples were collected in the Jânio Quadros Tunnel, which is a 1,900 m long tunnel located in the southeast region of the city of São Paulo, at a distance of 8 km from downtown. Its traffic is characterized by the circulation of light vehicles.

Two sampling campaigns were performed; the first one was held in June 2016 and, the second one, in October 2016. The dust samples were collected using clean polypropylene brushes and pans [9-11], taking extra care on the collection of the finest fractions. The sampling sites were located inside the tunnel, in its mid-section, and comprehended, separately, the traffic lanes (floor) and the pedestrian catwalk. Amounts of, approximately, 100 g each, were packed in clean polyethylene bags, and properly identified.

2.2. Analytical Procedure

At the laboratory, each sample was oven-dried at 60 °C (FANEM 315 SE), for about 12 h, and was sieved in stainless steel sieves into three different fractions: < 2 mm, < 150 μm and < 63 μm, generating a total of six sub-samples per sampling campaign. Next, the < 2 mm subsamples were grinded in an agate mortar, in order to obtain a fine and uniform dust, suitable for INAA.

Aliquots of 100-150 mg of each one of the sub-samples were weighted (Shimadzu Libror AEL-40SM) and sealed in 1 cm x 1 cm clean polyethylene envelopes. The same procedure was undertak-

en for the certified reference materials basalt BE-N and granite GS-N (SARM). All sub-samples and reference materials were, then, irradiated for 8 h at a thermal neutron flux of, approximately, 5 10^{12} n cm^{-2} s^{-1}, at the IEA-R1 nuclear research reactor, located at IPEN. The measurements of the induced gamma radiation were done in a gamma spectrometry system, which included a high purity germanium gamma ray detector (Canberra GX20190) and associated electronics. Each sample was measured twice: the first measure occurred 7 to 8 days after the irradiation and, the second one, 7 to 10 days after the first measurement. The quality control of the results was made by the analysis of certified reference material Soil-7 (IAEA), and the results showed relative errors lesser than 10% regarding the certified values.

3. RESULTS AND DISCUSSION

The results obtained for the mass fractions of the analyzed elements are presented in Table 1.

Table 1: Mass fractions (µg g^{-1}) and combined uncertainties (1σ) for REEs, U and Th in dust samples from the Jânio Quadros Tunnel.

Sampling Campaign	Site	Grain size	La	Ce	Nd	Sm	Eu
1st	**Floor**	**< 2 mm**	112 ± 12	247 ± 8	87 ± 15	15 ± 1	1.05 ± 0.02
1st	**Floor**	**< 150 µm**	16 ± 2	47 ± 1	13 ± 2	3 ± 0	0.69 ± 0.01
1st	**Floor**	**< 63 µm**	105 ± 12	239 ± 7	92 ± 6	16 ± 1	1.94 ± 0.15
1st	**Catwalk**	**< 2 mm**	52 ± 6	109 ± 3	35 ± 2	6 ± 0	0.84 ± 0.02
1st	**Catwalk**	**< 150 µm**	14 ± 2	29 ± 1	14 ± 2	2 ± 0	0.37 ± 0.02
1st	**Catwalk**	**< 63 µm**	38 ± 4	80 ± 2	30 ± 5	5 ± 0	0.90 ± 0.02
2nd	**Floor**	**< 2 mm**	14 ± 1	31 ± 2	15 ± 2	3 ± 0	0.54 ± 0.02
2nd	**Floor**	**< 150 µm**	165 ± 7	356 ± 28	137 ± 7	23 ± 3	2.05 ± 0.06
2nd	**Floor**	**< 63 µm**	137 ± 6	300 ± 24	114 ± 6	22 ± 3	2.04 ± 0.17
2nd	**Catwalk**	**< 2 mm**	36 ± 2	70 ± 6	31 ± 1	5 ± 1	0.78 ± 0.02
2nd	**Catwalk**	**< 150 µm**	57 ± 2	126 ± 10	47 ± 2	7 ± 1	0.92 ± 0.04
2nd	**Catwalk**	**< 63 µm**	37 ± 2	79 ± 6	28 ± 1	5 ± 1	0.87 ± 0.07

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Table 1 (continued)

Sampling Campaign	Site	Grain size	Tb	Yb	Lu	U	Th
1st	**Floor**	**< 2 mm**	1.81 ± 0.11	8.8 ± 1.4	1.000 ± 0.043	6.6 ± 0.6	30.8 ± 0.8
1st	**Floor**	**< 150 µm**	0.25 ± 0.03	1.0 ± 0.1	0.096 ± 0.005	1.0 ± 0.2	3.8 ± 0.1
1st	**Floor**	**< 63 µm**	1.71 ± 0.11	4.5 ± 0.5	0.840 ± 0.036	8.4 ± 0.7	35.9 ± 1.0
1st	**Catwalk**	**< 2 mm**	0.69 ± 0.05	2.1 ± 0.6	0.295 ± 0.013	3.5 ± 0.4	13.7 ± 0.4
1st	**Catwalk**	**< 150 µm**	0.22 ± 0.04	0.4 ± 0.1	0.063 ± 0.004	2.0 ± 0.2	3.3 ± 0.1
1st	**Catwalk**	**< 63 µm**	0.35 ± 0.04	1.7 ± 0.3	0.201 ± 0.010	3.7 ± 0.4	9.8 ± 0.3
2nd	**Floor**	**< 2 mm**	0.41 ± 0.07	2.7 ± 0.4	0.372 ± 0.044	1.5 ± 0.2	3.3 ± 0.1
2nd	**Floor**	**< 150 µm**	2.55 ± 0.32	6.9 ± 0.3	1.024 ± 0.066	7.3 ± 0.6	nd
2nd	**Floor**	**< 63 µm**	2.17 ± 0.28	4.5 ± 0.5	1.014 ± 0.130	9.0 ± 1.2	49.1 ± 2.6
2nd	**Catwalk**	**< 2 mm**	0.29 ± 0.09	0.7 ± 0.1	0.105 ± 0.007	1.8 ± 0.2	10.7 ± 0.6
2nd	**Catwalk**	**< 150 µm**	nd	0.8 ± 0.1	0.208 ± 0.040	3.4 ± 0.3	24.5 ± 1.3
2nd	**Catwalk**	**< 63 µm**	0.35 ± 0.09	1.4 ± 0.1	0.214 ± 0.025	1.7 ± 0.2	9.5 ± 0.5

nd = not detected

3.1. Seasonality, site of collection and grain size

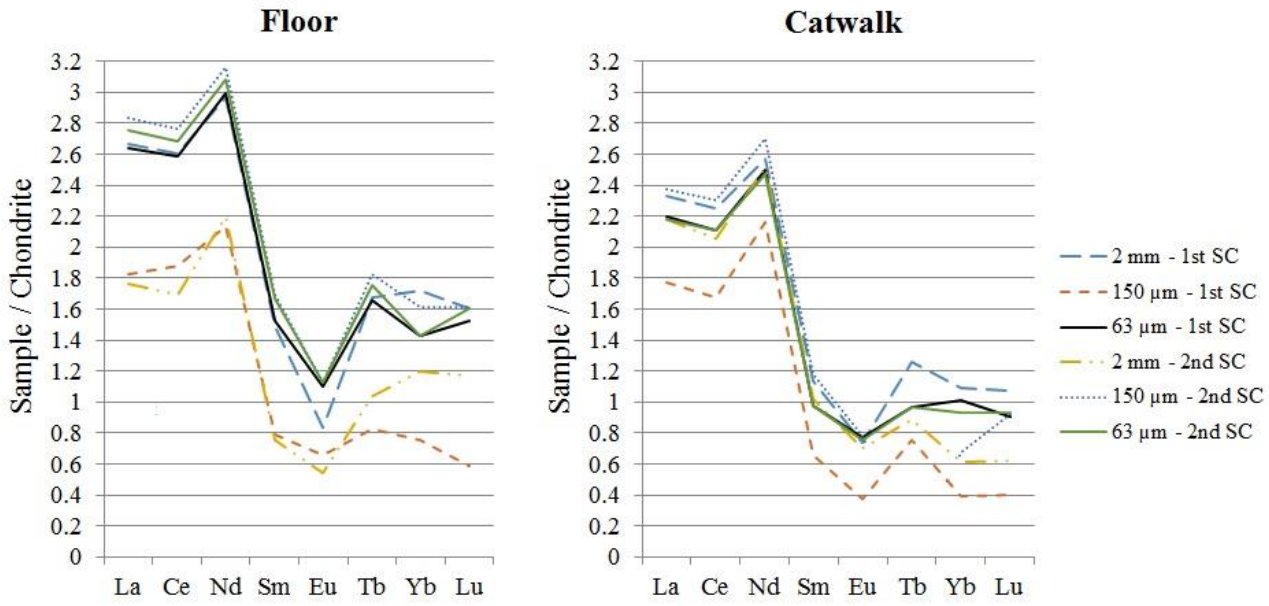
The obtained data were analyzed in order to assess the influence of seasonality, site of collection and grain size of the dust in mass fractions means. For the elements which presented normal distribution, Student's t-test (seasonality and site of collection) and ANOVA (grain size) were applied. For the others, the non-parametric Mann-Whitney (seasonality and site of collection) and Kruskal-Wallis (grain size) tests were applied. This statistical treatment showed that, for the majority of the analyzed elements, there were no significant difference in the mean values among sampling campaigns, sampling sites or grain size, at a significance level $\alpha = 0.05$. Specifically, differences were found only for Lu, Tb and Yb in relation to site of collection (higher means in floor samples) and for Sc in relation to grain size (higher mean in 63 µm samples).

3.2. Chondrite-normalized rare earth elements patterns

The analysis of the results showed that the mean mass fractions of these elements followed the sequence Ce > La > Nd > Sm > Yb > Eu > Tb > Lu. In order to display REEs abundances in the studied matrix, chondrite-normalized rare earth elements patterns are presented in Figure 1. Chondrite meteorites were chosen as a normalization factor since they are considered relatively non fraction-

ated samples from the solar system, related to original nucleosynthesis. This normalization eliminates natural abundance variation between even and odd atomic number elements and allows the identification of REEs fractionation in the analyzed samples.

Figure 1: *Chondrite-normalized REE patterns for the Jânio Quadros Tunnel dust (SC = Sampling Campaign)*



The results presented a pattern that evidenced higher concentrations of the LREEs in relation to HREEs, indicating that concentrations found are compatible to a crustal origin. Supporting this result, La/Ce ratios are approximately the same for all the analyzed samples and similar to that found for chondrites [12].

Europium presents a negative anomaly but, since there is no data for Gd concentrations, it could not be assured. An apparent enrichment of Nd was observed for all the analyzed samples. However, statistical analysis did not signalize any evidence of a possible additional source for this element, as will be discussed in the next section. This will be investigated in further studies.

3.3. Statistical analysis: possible origins of the elements in the studied environment

In order to better understand the relationship between elements, the data were also submitted to a multivariate statistics analysis – Principal Component Analysis (PCA). This analysis was made by using the IBM SPSS Statistics software, version 22, adopting the correlation matrix and varimax rotation. The results showed that the elements were grouped in, basically, one major group, as can be seen in the component matrix presented in Figure 2. The extracted component responds for, approximately, 87% of data variance.

Figure 2: *Component matrix*

Component Matrix[a]

	Component
	1
La	,984
Ce	,988
Nd	,985
Sm	,988
Eu	,927
Tb	,969
Yb	,850
Lu	,971
U	,965
Th	,615

Extraction Method: Principal Component Analysis

a. 1 extracted component - Kaiser criterion.

These results indicate that the elements have the same origin, probably crustal. There is no evidence of anthropogenic origin. In this environment, vehicle exhausts are expected to be the main contamination source, since atmospheric depositions play a minor role in REEs content in soils and similar matrices and tunnels are more protected from this influence because of its partial isolation from atmospheric wind flows and weather changes. In this case, enrichment in the concentrations of La, Ce and Nd, elements commonly found in automobile catalysts, would be expected.

4. CONCLUSION

In this study, the mass fractions of REEs, U and Th were determined by INAA in tunnel dust samples from the Jânio Quadros Tunnel, in São Paulo City. The results showed that the mean concentrations of the studied REEs follow the sequence Ce > La > Nd > Sm > Yb > Eu > Tb > Lu. The chondrite-normalized REEs patterns and multivariate statistics analysis suggested that these elements have the same origin in this environment, probably crustal. The results indicated that there was no evidence of anthropogenic contribution in REEs concentrations in the tunnel dust.

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