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DETERMINATION OF REE IN URBAN PARK SOILS FROM SÃO PAULO CITY FOR FINGERPRINT OF TRAFFIC EMISSION CONTAMINATION

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ABSTRACT

The study of rare earth elements (REE) distribution in urban environments has become very interesting in the last years, due to the increasing industrial use of these elements. The REE La, Ce and Nd are used in automobile converter catalysts to stabilize the catalyst support and to enhance the oxidation of pollutants. The honeycomb structure has a typical association of a high Ce (and often also La) concentration combined with high concentrations of Platinum Group Elements. Due to thermal and mechanical wear of catalysts, fine particles enriched in REE are released to the environment. These catalyst particles can accumulate in urban soils, mainly in soils located near high density traffic roads. The aim of this paper was to study the REE distribution and ratios in surface soil samples collected in fourteen urban public parks of São Paulo city, to assess the influence of vehicular emissions. Instrumental Neutron Activation Analysis (INAA) was used for the REE analysis. The diagrams normalized to chondrite values showed an enrichment of the light REE (La to Sm), in contrast to the heavy REE (Eu to Lu), with a negative anomaly of Eu. The results obtained indicated that the enrichment in REE is not clearly attributed to vehicular traffic, because of high background values associated to the natural geological composition of the soils.

1. INTRODUCTION

In addition to lanthanum (La), the lanthanides consist of the 14 elements following lanthanum: cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). Of these, Pm does not occur naturally in the environment. The rare earth elements (REE) include also the elements scandium (Sc) and yttrium (Y). The name "rare earth" is somewhat misleading, because these elements participate in the makeup of the earth's crust to a greater degree than others such as silver, cadmium or mercury. The abundance of Ce is almost the same as Zn and Cu. Their average abundance in the earth's crust range from 66 $\mu g\ g^{-1}$ in Ce to 0.5 $\mu g\ g^{-1}$ in Tm and $<<0.1\ \mu g\ g^{-1}$ in Pm [1]. Due to the successive filling in the 4f orbitals, the lanthanides are very similar in their physical and chemical properties. They all usually form trivalent cations. Technological uses of some of the lanthanides have increased in the last years. As components of alloys, Sm, Pr and Ce are used in magnetic materials, and La and Y serve as components of modern high-temperature superconductors. Others are used as catalysts for chemical reactions, or they are needed for the production of laser crystals. However, this increased industrial use also means that the lanthanides are present in higher levels in the environment. At the same time, only a little is known about the physiological effects of individual lanthanides on living organisms, so it is necessary for us to learn more about the natural concentration and the extent of the distribution of these elements in the environment.

The REE have neither been characterized as essential or toxic elements in the environment. Although much knowledge is available about physico-chemical properties and industrial applications, data on biological effects of REE are scarce. There are no indications that REE are essential to human and animals [1]. Until recently, their quantitative analysis in environmental samples was a difficult task. However, sensitive analytical techniques such as ICP-MS [2] and Instrumental Neutron Activation Analysis (INAA) [3] have proved their worth in such analysis.

REE concentration in surface soil vary according to parent material properties, history and weathering state of the soil, contents of organic matter and clay minerals, etc. Topsoil concentration may, therefore, differ considerably [1]. The use of REE in agriculture has been observed as a potential environmental problem in China [4]. The production and use of phosphate fertilizers may cause REE emissions both to the atmosphere and to the soils [5].

The study of the concentration and distribution of Platinum Group Elements (PGE) and REE in urban environment has increased in the last years due to their use in automobile catalytic converters. Cars fitted with exhaust catalysts containing platinum group elements significantly minimize toxic gas emissions produced during gas combustion. Catalysts remove about 90% of carbon monoxide, unburned hydrocarbons, and nitrogen oxides (NOx) from car exhaust and transform these pollutants into more innocuous carbon dioxide, nitrogen, and water [6]. The REE Ce, La and Nd, stabilize catalyst support (a γ-alumina based honeycomb) and enhance the oxidation of pollutants. However, catalytic converter surface abrasion and deterioration release these elements, adsorbed on small particles, emitted in the order of few ng km^{-1}, into the environment, causing PGE and REE deposits near roads, in vegetation, and in other environmental compartments such as rivers, as a result of wind and water transport. The composition and association present in these particles represent a characteristic fingerprint to distinguish autocatalytic particles [7].

Some elements are used as “tracers” to distinguish different sources of pollution. Elements such as Pb, Zn and Cu are considered traffic related, while Mn and V are associated to domestic emission. Particles derived from natural soil have typical REE pattern and ratios, similar to those of earth’s crust [7].

São Paulo is the biggest city in South America with a population of 19 million people. The urban area is polluted by industrial emissions but according to the Environmental Protection Agency of the State of São Paulo (CETESB), the governmental agency of air quality control, emissions from about 8.4 million motor vehicles daily are the main source of air pollution. The aim of this paper was to study the REE distribution and ratios in topsoils from fourteen urban public parks of São Paulo city, to assess the influence of vehicular emissions.

2. MATERIALS AND METHODS

2.1. Sampling Strategy

Fourteen public parks of São Paulo distributed allover the city were studied: Aclimação, Alfredo Volpi, Buenos Aires, Ibirapuera, Luz, Raposo Tavares, Tenente Siqueira Campos (Trianon), Guarapiranga, Raul Seixas, Rodrigo de Gáspari, Vila dos Remédios, Carmo, Chico Mendes and Cidade de Toronto Parks. Top soil samples (0-20cm) were composed by sub-samples collected in lines across the park every 30m. Sampling was performed in order to have representative samples of the entire park, mainly in sites where the flux of people was more intense, such as jogging paths, playgrounds and sport and leisure areas. A polyethylene tube with 4 cm diameter was used to take the samples, which were stored in inert plastic bags. In the laboratory, the samples were dried at 40-50oC and were sieved through plastic-only sieves into <2 mm fractions. Before and after sieving, the samples were homogenized and quartered. Samples were then ground using an agate mortar in order to obtain a fine and homogeneous powder (< 75 mm).

2.2. Analytical Methods

Instrumental neutron activation analysis (INAA) was the analytical technique employed. One hundred to one hundred and fifty mg of each sample and of the geological reference materials basalt BE-N (ANRT) and granite GS-N (ANRT) were accurately weighed in polyethylene bags. Samples and reference materials were irradiated for 8 hours at a thermal neutron flux of 1013 n cm-2 s-1 at the IEA-R1 nuclear reactor of IPEN. The measurements of the induced gamma-ray activity were carried out in gamma-ray spectrometer with a GX20190 hyperpure Ge detector (Canberra). The accuracy and precision of the results were verified by the analysis of the reference materials Soil-7 (IAEA). The results showed good accuracy (relative errors to certified values < 5%) and good precision (relative standard deviations < 10%).

3. RESULTS AND DISCUSSION

The REE concentrations in the fourteen parks studied are presented in Table 1, as well as the mean concentrations in the earth' crust. Table 1 shows a wide range of REE concentrations in the soil parks. The results obtained were much higher than the values considered as background concentrations in soils [8].

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. The results obtained and the earth's crust levels were normalized in relation to chondrite values as reference values (Figure 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. Except in Cidade de Toronto Park, a negative anomaly of Eu was observed. The REE, in most geological systems, form trivalent cations, though the divalent and tetravalent oxidation state is known for them in chemical compounds [1]. 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 withdraw 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.

Normalized REE show that REE distribution is related to natural background. The REE distribution patterns may be 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 cannot be attributed to vehicular sources, due to the high background values associated to the natural geological composition of the soils.

4. CONCLUSIONS

The results obtained for the REE concentrations in fourteen urban park soils of São Paulo did not show traffic-related REE enrichment because of high background values associated to the parent material. Nevertheless, the continuous use of REE in industries, fertilizers and catalysts requires REE monitoring in the environment.

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Table 1. Means and range concentrations of rare earth elements in public parks of São Paulo and earth crust (means) levels (mg kg^{-1})

Parks	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
Aclimação	37.0±7.3 27-45	70.0 ±12.7 50-87	23.5 ± 4.7 17-31	4.2 ±0.7 3.7-5.3	0.65 ± 0.11 0.5-0.74	0.72 ± 0.15 0.54-1.02	3.75 ± 0.74 2.7-4.7	0.62 ± 0.10 0.49-0.77
Alfredo Volpi	40.5 ± 16.1 23.7-82	85.4 ± 45.4 48-173	21.0 ± 12.2 11.8-44.5	4.26 ± 2.17 2.3-8.7	0.50 ± 0.09 0.37-0.55	0.59 ± 0.14 0.36-0.84	3.34 ± 1.06 1.85-6.0	0.43 ± 0.11 0.26 - 0.7
Buenos Aires	26.0 ± 2.7 23.2-28.5	56.1 ± 7.3 47.8-61.6	17.7 ± 1.5 16-19	3.2 ± 0.3 3.0-3.6	0.52 ± 0.04 0.49-0.57	0.53 ± 0.13 0.38-0.61	3.53 ± 0.06 3.5-3.6	0.57 ± 0.06 0.5-0.6
Carmo	12.7 ± 6.2 8.4-14.5	51.0 ± 27.6 24-101	6.5 ± 4.7 2.5-15	1.35 ± 0.38 1.07-1.85	0.20 ± 0.06 0.12-0.30	0.20 ± 0.12 0.06-0.36	1.7 ± 0.6 1.2-2.7	0.23 ± 0.04 0.20-0.31
Chico Mendes	30.7 ± 6.2 21.3-39.8	62.7 ± 14.0 39-80	15.0 ± 4.4 12-23	3.09 ± 0.65 2.23-4.04	0.46 ± 0.10 0.66-0.60	0.46 ± 0.05 0.39-0.52	2.62 ± 0.64 1.82-3.50	0.40± 0.11 0.27-0.55
Cidade de Toronto	61.9 ± 11.5 48.7-80.8	115.9 ± 12.2 100-139	48.1 ± 8.3 39-59	7.8 ± 1.1 6.3-9.8	1.85 ± 0.37 1.54-2.59	0.83 ± 0.14 0.59-0.98	1.86 ± 0.70 1.1-2.8	0.30 ± 0.09 0.18-0.45
Guarapiranga	50.4 ±19.6 22-73	130 ± 32 78-181	47.0 ± 18.3 18-75	8.05 ± 2.65 3.9-12.3	1.09 ± 0.65 0.37-2.2	1.27 ± 0.50 0.56-2.04	4.24 ± 1.82 1.7-7.8	0.535 ± 0.174 0.30-0.80
Ibirapuera	33.5 ± 7.2 25-46	72.9 ± 18.1 55-102	29.4 ± 9.0 12.0-46.5	4.85± 1.21 3.0-7.1	0.60 ± 0.23 0.43-1.15	0.81 ± 0.19 0.62-1.10	4.27 ± 1.01 3.0-5.7	0.65 ± 0.15 0.47-0.90
Luz	38.5 ± 9.8 22.5-56.9	83.9 ± 21.2 50-126	29.0 ± 8.5 16-45	5.73 ± 1.59 3.3-9.2	0.61 ± 0.17 0.46-1.04	0.78 ± 0.17 0.47-1.15	3.32 ± 0.50 2.1-4.3	0.51 ± 0.06 0.35-0.57
Raposo Tavares	26.6 ± 13.4 14.9-41	84.7 ± 31.3 48-132	20.8 ± 7.9 12-30	3.45 ± 1.48 1.8-5.3	0.507 ± 0.227 0.24-0.83	0.55 ± 0.23 0.23-0.81	2.95 ± 1.37 1.1-4.1	0.48 ± 0.18 0.22-0.62
Raul Seixas	10.6 ± 4.6 5.9-17.3	60.2 ± 26.9 29-93	5.4 ± 2.3 3.3-8.7	1.35 ± 0.50 0.88-2.13	0.22 ± 0.11 0.06-0.31	0.19 ± 0.15 0.02-0.41	1.26 ± 0.60 0.79-2.3	0.19 ± 0.08 0.13-0.32
Rodrigo de Gáspari	67.5 ± 11.9 48-85	144.8 ± 38.9 85-222	53.8 ± 12.0 34-68	8.8 ± 1.8 5.3-11.8	1.99 ± 0.46 1.04-2.72	0.76 ± 0.12 0.61-1.01	1.57 ± 0.39 1.1-2.3	0.35 ± 0.08 0.27-0.52
Trianon	20.9 ± 8.3 16.6-35	66.2 ± 55.4 31-174	24.5 ± 19.3 12-62	5.2 ± 4.3 2.5-13.4	0.615 ± 0.206 0.44-1.00	0.80 ± 0.79 0.18-1.00	7.0 ± 2.4 2.5-9.0	0.535 ± 0.233 0.38-1.00
Vila dos Remédios	54.2 ± 18.1 26.6-80	108 ± 32 68.6-153	34.1 ± 15.4 15.1-45	5.45 ± 1.90 3.1-8.3	0.90 ± 0.33 0.59-1.4	0.71 ± 0.20 0.32-0.88	2.82 ± 0.60 2.0-4.2	0.39 ± 0.04 0.37-0.47
Earth's crust (means)[1]	35	66	40	7.0	2.1	1.2	3.1	0.8
Background concentrations in soil [8]	5.0	9.0	40	0.7	0.1	0.1	0.6	0.11

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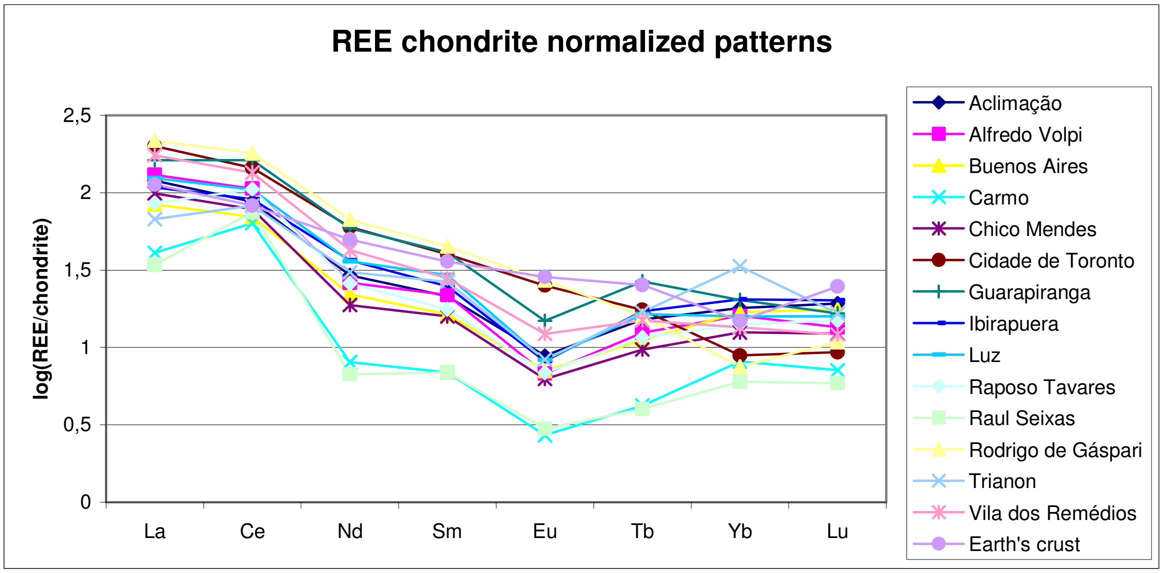

Figure 1. Chondrite normalized patterns for REE

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