

Determination of heavy metals and other trace elements in lake sediments from a sewage treatment plant by neutron activation analysis

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Instrumental neutron activation analysis (INAA) was used to determine metals (Ba, Co, Cr, Cs, Fe, Hf, Rb, Sc, Zn), semi-metals (As, Sb), actinides (U, Th) and rare earth elements (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) in bottom sediments from one of the ponds of the Sewage Treatment Plant (STP) in São Paulo, Brazil. The results obtained were compared with the concentration determined in a soil profile and in a rock sample, in natura, representing the lithologies of the region, and indicated that only As, Cr and Zn can have their origin associated with the residues disposed around the pond.

Introduction

São Paulo is the city with the largest population in Brazil (about 17 million) and is the main industrial center in Latin America. The Sewage Treatment Plant (STP) in Barueri, São Paulo, processes a significant amount of sewage generated in São Paulo city. Due to economic and technical problems, all the residual sludges produced at the STP from 1988 to 1996 were cumulatively disposed over the land, in piles and in open areas, deposited directly on the soil. The STP has two ponds, which were built to landscape the place, and one of them has half of its contour composed of residues of the STP's sewage sludge. The sewage sludge presents variable levels of several elements such as As, Cr, Fe, Cd, Cu, Ni, Pb, Mo, Co and Zn,¹ which may cause damage to soil, water and living organisms. The pond, which is the object of this study, is located in the residues' deposition area.

Instrumental neutron activation analysis (INAA) has been widely used to analyze sediments, which are well known as contamination monitors, due to the concentration of metals in aquatic environments.² In the present work, INAA was applied to determine metals (Ba, Co, Cr, Cs, Fe, Hf, Rb, Sc, Zn), semi-metals (As, Sb and Se), actinides (U, Th) and rare earths (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu), in bottom sediments from one of the ponds of the STP of Barueri. The aim was to study the contamination of this pond, by the transport of sewage sludge residues.

Experimental

Sampling procedure

The pond studied is inside the STP of Barueri and has an area of about 8000 m². The sampling stations

were distributed in a regular network, at about 50 m apart (Fig. 1), as recommended by MUDROCH and MACKNIGHT.³ The bottom sediments were fractionated in the field in terms of sub-samples of the top (3–5 cm) and the base of the core material. Samples were collected in different periods of the year (dry and wet), by using a modified Kajak-Brinkhust bottom grab, transferred to polyethylene bags, stored at 4 °C, transported to the laboratory and frozen at –20 °C.

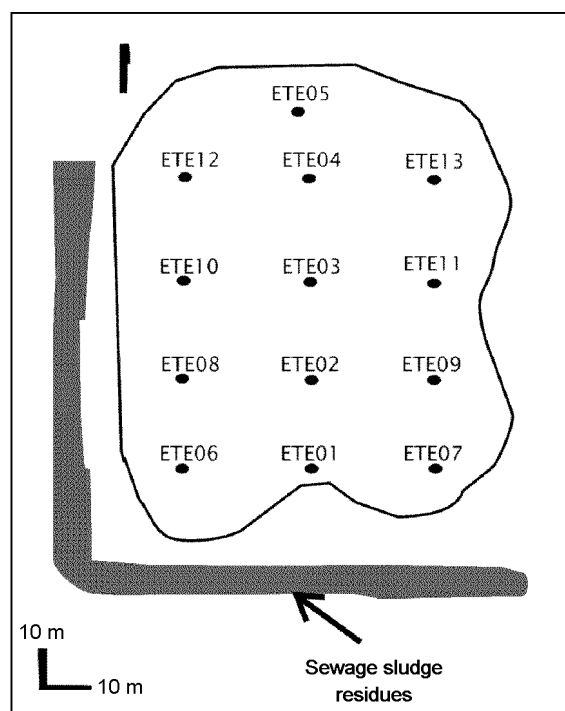


Fig. 1. Sampling stations

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In the west part of the pond, a rock *in natura* and a soil profile, 4 m depth, fractioned every 20 cm, that was representative of the lithologies of the region, were sampled. These samples were also stored in polyethylene bags.

Analytical procedure

Each sample of the sediments was split into two parts. One part was used for granulometric analysis (fraction <1.0 mm). For INAA, samples were dried at 40 °C in a ventilated oven for three days, were carefully ground in agate mortars and stored in polyethylene bags until analysis.

INAA

One hundred to one hundred fifty mg of the samples (bottom sediments, soil and *in natura* rock) was accurately weighed in polyethylene bags. Elemental synthetic standards of the analyzed elements were prepared by pipetting convenient aliquots of standard solutions (SPEX) onto 1 cm² pieces of Whatman No. 40 filter paper. The standards were then sealed in polyethylene bags. Samples and standards were irradiated for 16 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 a GMX20190 HPGe detector (Canberra). The multi-channel analyzer was a 8192-channel Canberra S-100 unit (plug-in-card in a PC). The resolution (FWHM) of the system was 1.90 keV at the 1332 keV gamma-ray of ⁶⁰Co. Two spectral measurements were obtained: the first one was obtained 5 days after irradiation and the second one was obtained 15 days after irradiation. The counting times varied from 1 to 2.5 hours. The gamma-ray spectra were processed by using the VISPECT gamma-ray software,⁴ which locates peak positions and calculates the energies and net areas. The accuracy and precision of the method was previously verified by analyzing the reference materials Buffalo River Sediment (NIST SRM 2704) and Estuarine Sediment (NIST SRM 1646a).⁵

Results and discussion

The concentrations of 24 elements were determined in 41 samples, representing the sediment samples collected in the two periods of sampling (wet and dry), the soil profile, and the rock *in natura* samples.

Table 1 presents the concentration range of the analyzed sediments in the superficial fraction, as well as the mean concentrations obtained for these samples. The

mean values obtained for the soil profile are also presented, wherein it is assumed that there was no variation in soil values at the different depths. This procedure facilitated the comparison of the results observed in the sediments and those obtained for the soil profile and the rock, and also the values of the mean concentration in sedimentary rocks, i.e., the shale.⁶ The comparison with shale values is a well known method used to verify if a particular element may be considered "natural". However, this method imposes some restrictions, since the sedimentary rocks used for comparison may be very different from the rocks found in tropical countries. Results compared with the concentration obtained in the soil profile and in the rock gives a more realistic assessment of the environment studied, since a correlation may be made with the concentration obtained in the sediments and the lithologies of the region.

With respect to elemental concentration levels in shale, the results obtained for Ba, Hf, Mo, Th, Zn and rare earth elements (REEs) indicate contamination. Elements such as Cs, Hf and Rb may be considered as having originated from the neighboring lithologies, if the concentration values in the soil and in rock are observed. The high values obtained for REEs suggest that the source of these elements is the granite rock formations of the Complexo de Itaquí, located near the aquatic environment.⁷ Regarding granulometric analysis, the sediment samples representing the fines are between 80% and 100% in most of the top sediment samples. No statistical test was applied correlating the concentration observed in sediments with the fines percentage, since this procedure would not provide relevant information in this study.

Pearson's correlation applied to the values obtained in the different sampling stations ($r > 0.999$) in the dry period showed a uniform distribution of all analyzed elements among the stations, indicating that there is no contaminant concentration near the sludge deposits. With respect to elemental concentrations corresponding to the sampling points, Pearson's correlation also showed that the sediments present the same characteristics in all the sampling stations, regardless of any concentrating effects. On the other hand, according to the adopted contamination criteria (comparison to shale, soil profile and rock concentration values), most of the elements analyzed may be considered to have a natural origin.

The concentration values observed for As are within the range accepted for the shale. Nevertheless, significant As concentration in the sediment may indicate an anthropogenic origin, since the soil profile analysis showed that As is not concentrated along it (essentially uniform).

Table 1. Results obtained for sediment, soil profile and rock sample (in $\mu\text{g g}^{-1}$)

Element	Concentration range, $\mu\text{g g}^{-1}$			Mean concentration, $\mu\text{g g}^{-1}$			Shale	Mean concentration in soil profile, $\mu\text{g g}^{-1}$			Rock in nature
	Top sediment (dry period)	Top sediment (wet period)	Top sediment (dry period)	Top sediment (dry period)	Top sediment (wet period)	Top sediment (wet period)		Mean concentration in soil profile, $\mu\text{g g}^{-1}$			
								(0.9–1.0 m)	(1.5–2.4 m)	(3.0–4.2 m)	
As	2.4–5.3	0.5–2.7	4 ± 1	726 ± 136	2 ± 1	732 ± 254	13	N.D.	N.D.	N.D.	8.5 ± 0.4
Ba	585–945	318–1357	726 ± 136	17 ± 3	21 ± 13	732 ± 254	580	953 ± 53	920 ± 106	655 ± 47	592 ± 6
Co	13–54	13.7–61	17 ± 3	77 ± 10	76 ± 13	21 ± 13	19	7.2 ± 0.2	14 ± 4	9 ± 1	4.9 ± 0.3
Cr	58–89	40–90	77 ± 10	6 ± 1	5 ± 1	76 ± 13	90	18.6 ± 0.5	42 ± 4	49 ± 11	12 ± 1
Cs	4.4–9.0	3.7–7.5	6 ± 1	4.7 ± 0.4	5 ± 1	5 ± 1	5	3.0 ± 0.4	7 ± 10.1	3.3 ± 0.4	2.8 ± 0.4
Fe, %	3.6–5.2	2.7–5.5	4.7 ± 0.4	7 ± 3	7 ± 3	5 ± 1	4.7	1.7 ± 0.1	3.5 ± 0.1	3.6 ± 0.4	1.80 ± 0.03
Hf	2.8–13.0	2.8–11.9	7 ± 3	5 ± 3	9 ± 1	7 ± 3	2.8	10 ± 1	13 ± 1	15 ± 1	7.0 ± 0.4
Mo	2.5–11.6	7.9–9.9	5 ± 3	143 ± 33	159 ± 41	9 ± 1	2.6	4 ± 1	N.D.	3 ± 1	4.6 ± 0.8
Rb	88–189	98–232	143 ± 33	0.95 ± 0.39	0.8 ± 0.3	1.59 ± 0.41	140	138 ± 1	223 ± 43	132 ± 45	251 ± 10
Sb	0.21–1.3	0.46–1.49	0.95 ± 0.39	15 ± 1	15 ± 3	0.8 ± 0.3	1.5	0.082	0.14 ± 0.01	0.11 ± 0.01	0.30 ± 0.03
Sc	12–16	7.6–16.3	15 ± 1	0.9 ± 0.6	0.8 ± 0.6	15 ± 3	13	4.3 ± 0.2	9.5 ± 0.2	10.4 ± 0.4	10.7 ± 0.4
Se	0.34–1.6	0.4–2.0	0.9 ± 0.6	1.7 ± 0.4	1.5 ± 0.3	0.8 ± 0.6	0.6	1.07 ± 0.04	1.3 ± 0.1	1.8 ± 0.1	1.2 ± 0.1
Ta	1.3–2.9	1.0–2.0	1.7 ± 0.4	31 ± 8	29 ± 3	1.5 ± 0.3	1.8	1.20 ± 0.04	1.6 ± 0.1	2.5 ± 0.2	0.48 ± 0.03
Th	25–32	19.6–31.1	31 ± 8	6 ± 1	4 ± 2	29 ± 3	12	51 ± 1	40 ± 2	37 ± 6	27 ± 1
U	4.0–7.0	2.1–7.9	6 ± 1	134 ± 29	128 ± 28	4 ± 2	3.7	4.1 ± 0.5	4.4 ± 0.6	4 ± 1	7 ± 1
Zn	95–174	68–170	134 ± 29	192 ± 34	151 ± 25	128 ± 28	95	55 ± 5	115 ± 25	58 ± 20	59 ± 4
La	138–227	105–179	192 ± 34	184 ± 36	190 ± 50	151 ± 25	92	177 ± 9	262 ± 50	249 ± 71	55 ± 3
Ce	133–257	102–265	184 ± 36	125 ± 29	100 ± 31	190 ± 50	80	288 ± 21	217 ± 6	374 ± 66	86 ± 1
Nd	96–188	56–160	125 ± 29	24 ± 4	19 ± 3	100 ± 31	24	109 ± 9	179 ± 20	162 ± 27	43 ± 3
Sm	16–31	17.0–25.1	24 ± 4	4 ± 1	4 ± 1	19 ± 3	6.4	20 ± 0.4	29 ± 7	29 ± 6	11.9 ± 0.3
Eu	2.7–5.0	2.8–5.0	4 ± 1	1.7 ± 0.2	1.9 ± 0.3	4 ± 1	1.0	2.4 ± 0.1	4.8 ± 0.4	4.4 ± 0.4	1.10 ± 0.02
Tb	1.4–2.1	1.60–2.7	1.7 ± 0.2	4 ± 1	3.5 ± 0.8	1.9 ± 0.3	1.0	1.4 ± 0.2	2.2 ± 0.1	3 ± 1	1.0 ± 0.1
Yb	2.9–5.5	2.4–4.7	4 ± 1	0.6 ± 0.1	0.6 ± 0.2	3.5 ± 0.8	2.6	2.3 ± 0.2	4.4 ± 0.8	5 ± 1	4.6 ± 0.1
Lu	0.50–0.70	0.44–0.93	0.6 ± 0.1	0.6 ± 0.1	0.6 ± 0.2	0.6 ± 0.2	0.7	0.4 ± 0.04	0.65 ± 0.05	0.7 ± 0.1	1.0 ± 0.1

N.D.: Not determined.

The Student *t*-test at the 95% confidence level showed that the concentrations of the analyzed elements do not differ significantly from one period to another, except for As. Figure 2a provides the distribution of As in the sampling stations and indicates that the concentration of As was higher in the dry period. Since rain water is the only (or, at least, the most important) agent for transporting sedimentary deposits to the pond, this fact suggests that As is transferred to the pond during the wet period, remains in suspension and is subsequently deposited in the sediment during the dry period. This assessment suggests that As originated from the sewage sludge deposited around the pond. The results obtained for Co (Fig. 2b) in stations 04 and 08 may be considered anomalous.

In most of the sampling stations, the results obtained for Zn (Fig. 2c) in the superficial fraction of the sediment were higher than in shale, indicating contamination due to sewage sludge. On the other hand, the data indicate that Zn tends to concentrate along the soil profile, provided that its concentration in the rock is about 60 mg·kg⁻¹ compared to a mean soil concentration of 115 mg·kg⁻¹. According to ASSUNÇÃO and SÍGOLO,¹ Cr and Zn displayed concentrations up to 910 mg·kg⁻¹ and 2750 mg·kg⁻¹ (dry weight), respectively, in the

residue deposited around the pond. In the same study, both Cr and Zn were detected in the base of the residue pile. This behavior indicated that these elements migrate from the residue to the environment, mostly from the top of the residue pile. On the other hand, Cr and Zn displayed the lowest solubility in a chemical extraction with hot deionized water (<1% of the total), which represents the most available forms to the environment. Therefore, it can be concluded that the distribution pattern of Zn may associate its origin both from natural and anthropogenic sources.

Cr (Fig. 2d), like As, displayed concentration levels in accordance with the shale levels, but its concentration in the top sediment was considerably higher than those obtained in the rock and in the soil profile, indicating that its origin may be related to the sewage sludge residue. According to ASSUNÇÃO and SÍGOLO,¹ this behavior in the residue pile was similar to that of Zn, thereby indicating an anthropogenic origin.

The concentrations of the elements As, Co, Cr, Sb and Zn in the superficial and base fractions were normalized to the Sc concentration obtained at each sampling station during the dry period. Sc was chosen as the conservative reference element due to its highly favorable nuclear characteristics for INAA.⁸

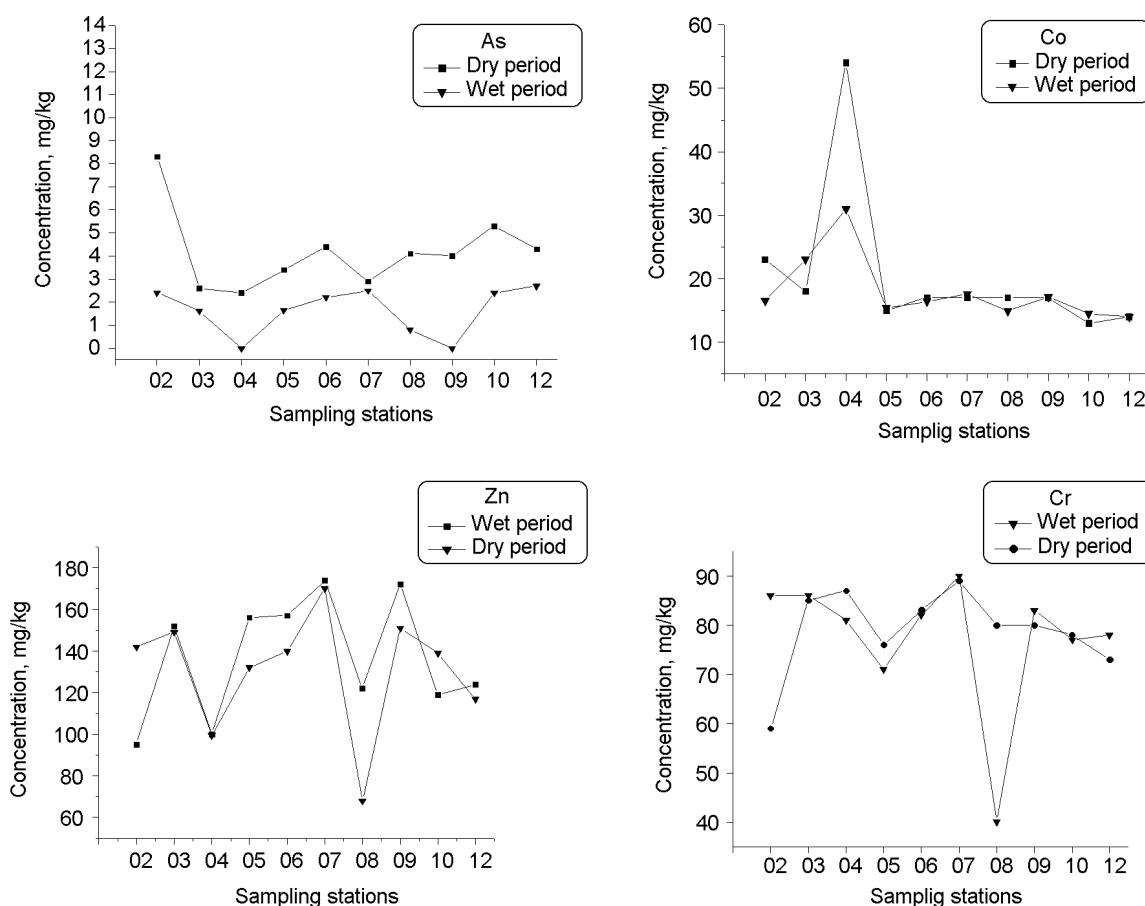


Fig. 2. Concentration pattern of As, Co, Zn and Cr in the superficial fraction of the sediment

Table 2. Concentration values normalized to Sc concentration in each sampling station

Sampling station	[As]/[Sc] (dry period)	
	Top	Base
01	0.22 ± 0.01	0.30 ± 0.02
02	0.7 ± 0.1	0.08 ± 0.01
03	0.16 ± 0.01	0.09 ± 0.01
04	0.16 ± 0.01	0.5 ± 0.1
06	0.29 ± 0.01	0.09 ± 0.02
12	0.31 ± 0.01	1.0 ± 0.2
05	0.23 ± 0.01	0.7 ± 0.1
07	0.19 ± 0.01	0.9 ± 0.2
08	0.27 ± 0.01	0.9 ± 0.1
10	0.33 ± 0.01	1.2 ± 0.2

Sampling station	[Cr]/[Sc] (dry period)	
	Top	Base
01	4.83 ± 0.02	5.00 ± 0.02
02	4.8 ± 0.4	5.00 ± 0.02
03	5.3 ± 0.4	5.33 ± 0.02
04	5.80 ± 0.02	6.1 ± 0.4
06	5.5 ± 0.5	5.0 ± 0.3
12	5.2 ± 0.5	6.0 ± 0.4
05	5.1 ± 0.1	5.0 ± 0.3
07	6.0 ± 0.5	4.0 ± 0.3
08	5.3 ± 0.5	5.0 ± 0.3
10	5.0 ± 0.4	5.3 ± 0.3

Sampling station	[Sb]/[Sc] (dry period)	
	Top	Base
01	0.03 ± 0.01	0.05 ± 0.01
02	0.017 ± 0.001	0.018 ± 0.001
03	0.063 ± 0.001	0.033 ± 0.003
04	0.040 ± 0.001	0.006 ± 0.001
06	0.09 ± 0.01	0.022 ± 0.003
12	0.07 ± 0.01	0.062 ± 0.003
05	0.07 ± 0.01	0.027 ± 0.003
07	0.08 ± 0.01	0.013 ± 0.002
08	0.09 ± 0.01	0.033 ± 0.002
10	0.06 ± 0.01	0.018 ± 0.001

Sampling station	[Co]/[Sc] (dry period)	
	Top	Base
01	1.2 ± 0.1	0.95 ± 0.03
02	1.9 ± 0.2	1.2 ± 0.1
03	1.1 ± 0.1	2.5 ± 0.1
04	3.6 ± 0.1	2.8 ± 0.2
06	1.1 ± 0.1	1.4 ± 0.1
12	1.0 ± 0.1	2.4 ± 0.2
05	1.0 ± 0.1	1.3 ± 0.1
07	1.1 ± 0.1	2.3 ± 0.3
08	1.1 ± 0.1	1.0 ± 0.1
10	0.8 ± 0.1	1.6 ± 0.2

Sampling station	[Sb]/[Sc] rate (dry period)	
	Top	Base
01	0.03 ± 0.01	0.05 ± 0.01
02	0.017 ± 0.001	0.018 ± 0.001
03	0.063 ± 0.001	0.033 ± 0.003
04	0.040 ± 0.001	0.006 ± 0.001
06	0.09 ± 0.01	0.022 ± 0.003
12	0.07 ± 0.01	0.062 ± 0.003
05	0.07 ± 0.01	0.027 ± 0.003
07	0.08 ± 0.01	0.013 ± 0.002
08	0.09 ± 0.01	0.033 ± 0.002
10	0.06 ± 0.01	0.018 ± 0.001

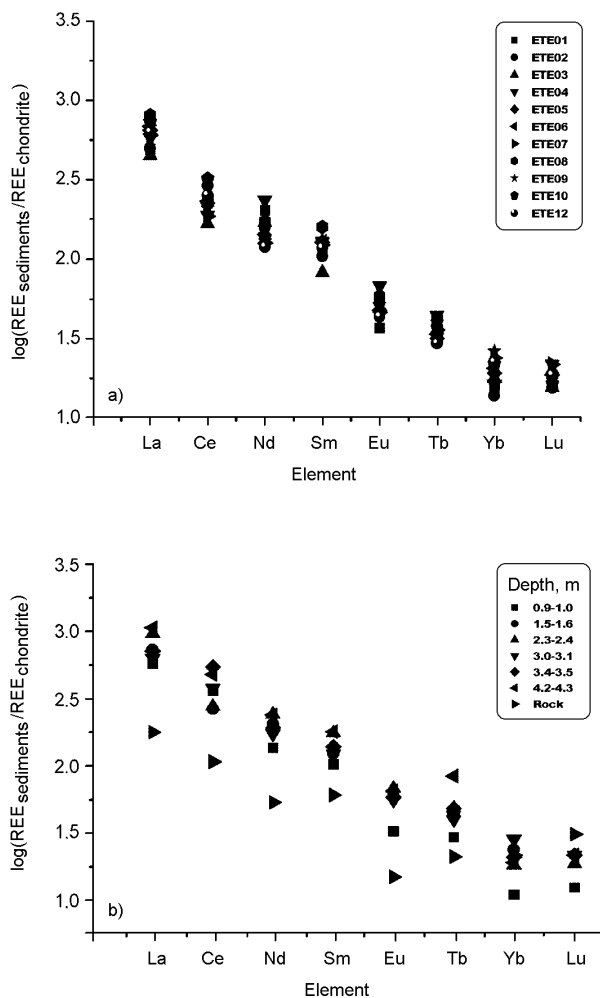


Fig. 3. REE concentrations in the superficial fractions of the sediments in dry period (a) and in the soil profiles and in the rock in natura (b) normalized to chondrites

It can be seen (Table 2) that Co/Sc, Cr/Sc and Sb/Sc rates were essentially constant across the sediments analyzed. On the other hand, the Zn/Sc rate was higher in the superficial fraction in almost all sediments analyzed, thereby indicating contamination. The As/Sc rate did not show the As origin associated with sludge residue.

Rare earth elements

The concentrations obtained for the rare earth elements (REEs) in the sediment samples, in the soil profile and in the rock sample were normalized in relation to chondrite concentration.¹⁰ The distribution pattern obtained for REE in the top sediment showed a higher concentration of light rather than heavy REEs, thus presenting a typical granite rock pattern,¹⁰ similar to the results obtained by FERREIRA⁷ in the rocks from

Complexo de Itaquí (Fig. 3a). The same distribution pattern was observed in the soil profile (Fig. 3b). These results indicated that the origin of REEs is related to the lithologies of the region and not to anthropogenic activities. The concentrations of U and Th may also be associated with the granites of Complexo de Itaquí.

Conclusions

Considering that the analyzed samples were obtained from a Sewage Treatment Plant, and that the residual sewage sludge had accumulated for ten years around the pond studied, it was expected that the concentration of most elements analyzed was significantly higher than the values in shale. However, it was observed that only the elements As, Cr and Zn may be considered as having originated from the sewage sludge.

The results obtained in this study provided valuable information for monitoring contamination in the pond of the Sewage Treatment Plant of Barueri and demonstrated that INAA is a very useful tool for environmental studies of pollution.

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