Trace and major elements in geological samples from Itingusssú River Basin, Sepetiba Bay—Rio de Janeiro

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Abstracts The Itingussú drainage basin is situated at $22°44^0$–$22°55^0$ SL and $44°53^0$–$43°55^0$ WL, in Coroa-Grande district, Sepetiba Bay, southwest of Rio de Janeiro, Brazil. Its total area is less than 10 km^2 and includes a waterfall with three drop offs. The study area is located in a granitic pre-Cambrian embasement, discharging in a mangrove forest fringe. This work attempts to investigate the influence of lithology types in the elemental composition of soil of region and sediments of related mangrove. Instrumental neutron activation analysis and subsequent gamma-ray spectrometry were used. This technique enabled the measurement of at least twenty-one chemical elements. The more representative soil samples were enriched with U and Th. Multivariate Statistical Analysis showed that the soil and sediments formed in this area have been influenced by the leucocratic rocks, enriched with LREE and Th. The factorial analysis enables the identification of five factors of influence in the ordination of elements: presence of iron minerals (biotite); presence of allanite; marine influence in the sediment; differentiated kinetic of transport and diagenesis.

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Introduction

The mangrove ecosystem involves an important role in hydrodynamic stability of the marine coast of tropical countries. It can act as a sink of continental material, as well as allowing exportation of soluble chemical substances to the sea [1]. Their muddy soils are density covered by vegetation composed of species including *Rizophora spp* and *Avicennia spp*. The soil contains abundant organic matter, water saturation and strong reducing conditions. It is rich in pyrite, iron and manganese oxihidroxides which plays an important role in the accumulation of several chemical trace species, such as zinc, iodate, phosphate, mercury, etc. [2–7]. These natural records allow identifying the chemical processes related to this environmental, including the anthropogenic impact [8, 9].

Since the 80's several studies have been carried out in the Sepetiba mangrove area to understand the urban and industrial impact of the region [10–23]. All of these studies have discussed the anthropogenic influence related to the livestock and agricultural activities, ore transportation to the navy port in the east of the Bay, associated with waste production from the nuclear power plants located further west in the Angra dos Reis district [24–26]. Nevertheless, until now there is no quantitative knowledge about the influence of the lithology in that area may support discussions on the anthropic influences in respect to some

elements that were actually at issues, such as rare earth elements and uranium. In a previous work, the present authors [27] have analysed rock samples collected in the Itingussú basin, located in the meadow of the Sepetiba Bay; this work has allowed the classification eight litho-types from this area: dioritic-quartz, tonalitic gneiss, leu-cogranite, quartz-dioritic gneiss, granodioritic gneiss, diabases and leucotonalite. The chemical composition of it included about of 23 elements, determined by using the nuclear analytical technique of neutron activation analysis (INAA). In this accordance, the present work is intended to characterize the chemical signature of the soils and sedi-ments of the Itingussú area in order to investigate the influence of the lithology on these geological samples.

Materials and methods

Site study and sample collection

The Itingussú Basin is situated at $22°44^0$–$22°55^0$ SL and $44°53^0$–$43°55^0$ WL, and belongs to Coroa-Grande district, Sepetiba Bay, south of Rio de Janeiro. The Bay is less than 10 km^2. The local soil, not being well developed, is classified between cambissol and latossol [28], composed of rock altered and red clay, with a little O horizon. Alterite samples were collected from C and B horizon of fresh cuts, from a recent urban developing area. Rework banks of clay were avoided, and only one of this type of sample was collected (named A3.0). Others soil samples were saprolites, isoalterites and schist. Three sediments cores were collected from the mangrove area with 30 cm height, using polyvinylchloride tube of 6 cm internal diameter. The core named *Iting* belongs to the site in the upper zone of the mangrove, surrounding the Itingussú River. The second core was collected in a tidal creek, named *Itacuruçá Creek* (CN), to assess the contribution of marine source; and a third core was collected in the *mangrove's forest* (FL), which is further west from Itingussú River. The forest has suffered only a pluvial and percolation water influence [29].

The Fig. 1 shows some details of the Itingussú River drainage basin and Table 1 the denomination and description of the collected samples. Site descriptions were made elsewhere, in the previous work already cited [27].

Sample pretreatment

The soils samples were powdered and sieved in 2 mm inox sieves. The roots and little graves were discarded. So, the samples were quarted in a plastic manual quarter. The cores of sediment were initially sliced in 1 cm for the first 5 cm from the top; and afterward in 2 cm thick along the tube. These fractions were dried, powdered in an Agatha graal and sieved to 2 mm size, after this it's quarted in the same way of the alterites (Table 2).
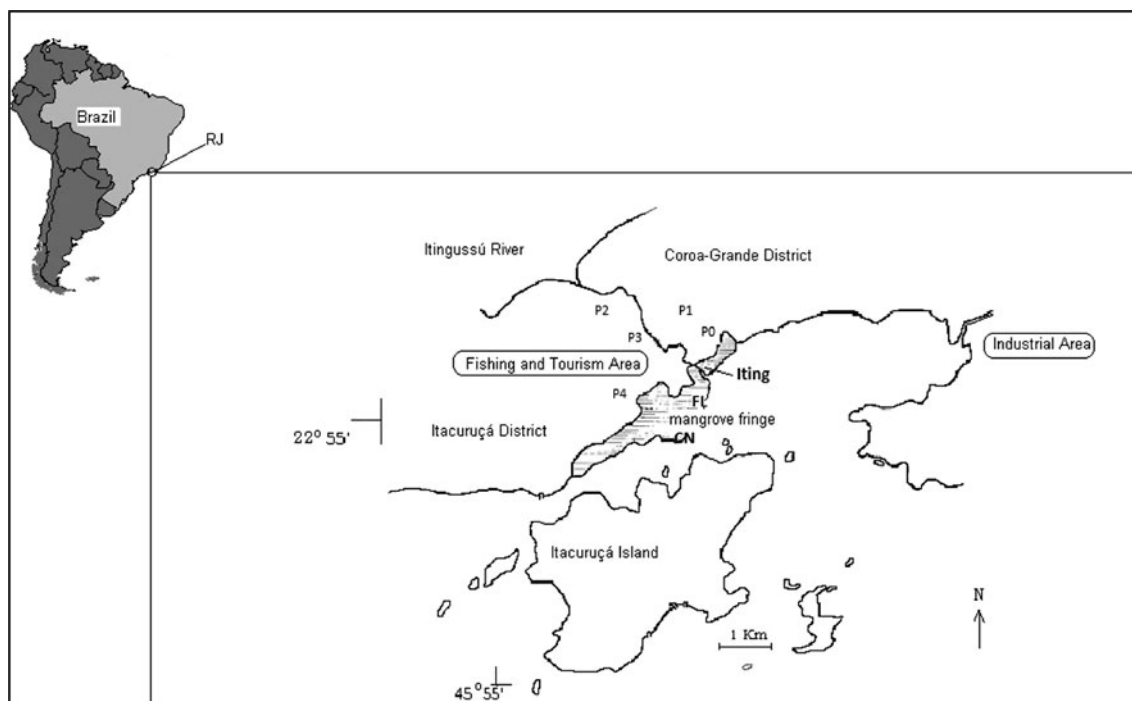

Fig. 1 Sample sites in the Itingussú area

Table 1 Denomination and field description of the samples collected

Sample	Site	Sample description
Alt1	P0	Alterite
Alt2	P0	Alterite collected close to a saprolite
R13	P0	Saprolite
A1.0	P1	Saprolite
A1.1	P1	Isoalterite
A2.1	P2	Most alternated diabase
A2.2	P2	Alterite of diabase
A3.0	P3	Mixing of reworked alterite
A4.1	P4	Saprolite
A4.2	P4	Schist vein
A4.3	P4	Isoalterite of schist
FL	Itacuruçá Forest	More closed mangrove, influence of meteoric water
		Core with many roots, more oxidized, brow colour
Iting	Itingussú River	Darker and homogeneous core of sediment
CN	Canal creek	Oxidized sediment, more arenous, with sand and shells in this core

Table 2 Concentration of major elements (%) and trace elements (mg kg^{-1}) in used standards in the INAA

Elementos	BCR1 [32]	PODMORE [30, 31]	SOIL-7 [33]	SRM2704 [34]
Al (%)	7.21	11.44	4.70	6.11
Ba	678	442.4	159	414
Ca (%)	–	1.9	16.3	2.6
Ce	53.7	65.5	61	72
Co	36	21.2	8.9	14
Cr	16.2	123.2	60	135
Cs	0.97	14.21	5.4	6.0
Dy	6.35	6.13	3.9	6.0
Eu	1.97	1.56	1.0	1.3
Fe (%)	9.38	5.22	2.57	4.11
Hf	4.9	6.53	5.1	8.0
La	26	41.34	28	29
Lu	0.52	0.30	0.30	0.60
Mg	20865	9360	11300	12000
Mn	1394	404.9	631	555
Na	24260	686	2400	5470
Nd	29	–	30	–
Rb	47	85.2	51	100
Sb	0.62	0.752	1.7	3.79
Sc	33	24.08	8.3	12
Sm	6.6	7.35	5.1	6.7
Tb	1.0	–	0.6	–
Th	6.4	12.4	8.2	9.2
Ti	12589	6789	3000	4570
U	1.72	3.05	2,6	3.13
V	401.5	152	66	95
Yb	3.36	3.6	2.4	2.8

Obs (–) not used or not certified value

Activation analysis

The comparative method was used in the instrumental neutron activation analysis (INAA). Therefore, each sample with their corresponding standard was weighted around 200 mg and irradiated at the AIEA-R1 reactor of the Institute of Nuclear Energy and Research (IPEN), Brazil. The standard used to the alterites was the clay named as PODMORE [30, 31], with an exception to the maphic alterites, for that it was necessary to use the basalt BCR1 [32]. To the analysis of the sediments it was employed two standards: Soil-7 (IAEA) [33] and Buffalo sediment (NIST) [34], according to the nature of chemical matrix.

The irradiations were carried out with a neutron flux of 10^{12} cm^{-2} s^{-1}. For short-lived radionuclides the irradiation time was 1.5 min and the samples counted for 4 min; for long-lived radionuclides the irradiation time was 8 h and after 10 days of cooling time the samples were counted for 5400 s.

Detection and measurement system

The irradiated samples were counted in the coaxial detectors ORTEC⁰s high purity Ge detector (GeHP), and also in CAMBERRA⁰s low energy photon detector (GAMX). The resolution for the 1332.5 keV gamma ray of ^{60}Co was 2.8 and 1.8 keV respectively. The same counting geometry was used for samples and standards.

The gamma-ray spectra was analysed with the GRGAN code; this programme allow choosing the background of each photopeak, which was specially selected to be free of interferences [35–37]. The spectra collected with the Canberra system (Genie2 k) were converted to a CHN format with a programme written specially for this purpose [38], and so it was analysed by the GRGAN program.

Statistical treatment

Multivariate statistical packet *Statistica 5.0* was used and Pearson correlation test was applied to the data matrix to verify the correlation between the elements. Afterwards, the data matrix was normalized and used to obtain the clusters through Wards subroutine method of analysis (minimum variance). The Principal Component Analysis was also applied, to relating the elements with the ranking factors of them. Finally, the reduced composition data of soil, mangrove sediments and rocks was employed in the z-scoring method in order to verify the signature of these

Table 3 Concentration of major elements (%) and trace elements (mg kg^{-1}) in soils by INAA

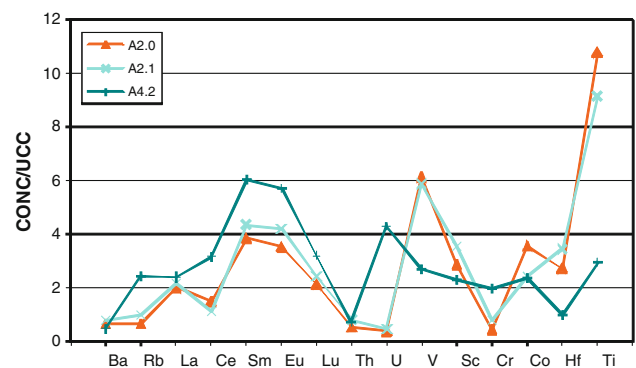|	A1.0	A1.1	A2.0	A2.1	A3.0	A4.1	A4.2	A4.3	ALT1	ALT2
Na (%)	0.200	0.160	0.0515	0.187	0.124	0.143	0.0288	0.0535	0.0703	0.176
Mg (%)	0.907	0.936	0.700	0.504	0.693	0.600	1.58	1.37	0.856	1.05
Al (%)	11.3	10.7	(9)	(11)	9.11	5.31	9.82	12.3	9.16	8.87
Fe (%)	2.23	3.90	13.6	16.3	3.29	0.648	10.3	417	4.62	4.17
Ti(%)	0.366	0.464	3,49	2.96	0.277	0.0601	0.948	0523	0.490	0.427
Mn	214	245	2186	985	224	97.8	995	392	206	299
V	47.0	70.3	526	505	33.3	8.77	230	91.0	68.2	65.5
Ba	1055	735	416	499	568	232	(308)	455	502	939
Cs	6.83	11.0	4.30	6.07	12.1	5.59	16.4	15.0	10.2	14.3
La	57.0	57.0	58.4	63.2	25.1	13.9	69.5	51.4	68.6	46.3
Ce	76.0	108	88.0	66.9	66.8	13.9	189	52.0	152	88.7
Sm	9.40	12.0	18.6	21.0	4.16	3.54	29.2	16.3	16.1	14.6
Eu	1.37	1.57	3.71	4.42	0.585	1.29	5.98	3.05	1.84	1.91
Dy	3.88	3.39	11.4	12.1	1.71	2.73	20.1	11.7	6.05	5.76
Sc	8.98	13.0	38.5	47.3	8.95	1.99	30.8	11.0	13.1	17.2
Cr	22. 5	42.1	49.7	89.8	30.3	(1.94)	220	93.1	47.7	63.4
Co	14.3	12.6	64.1	43.4	7.20	2.37	42.6	16.3	12.1	12.6
Rb	135	164	57.1	85.3	177	126	213	208	124	179
Sb	0.253	0.594	0.236	0.354	0.641	0.279	0.796	0.688	0.388	0.660
Lu	0.170	0.249	0.727	0.824	0.127	0.133	1.08	0.515	0.441	0.424
Hf	7.15	11.4	12.0	15.2	11.5	3.69	4.42	6.63	10.0	9.66
Th	15.1	25.7	4.74	7.40	18.1	13.0	6.52	3.82	34.1	29.5
U	3.51	4.45	0.913	1.14	3.66	2.78	10.3	2.19	8.10	6.66

Semiquantitative values are given in parenthesis
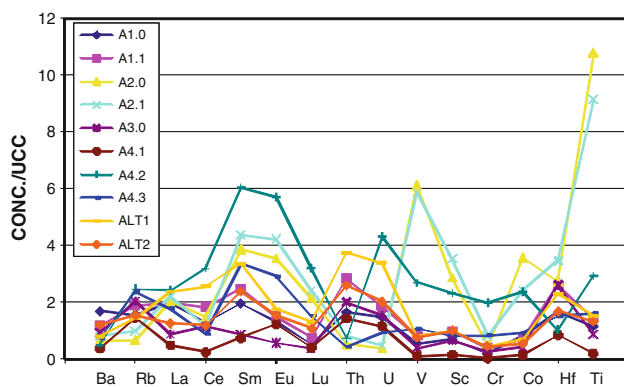
Fig. 2 Normalized values for trace elements in soil samples

Fig. 3 Normalized values for trace elements in soil samples—mafic rocks

three types of geological samples and the relationship between them.

Results and discussion

The mean elemental concentration for soil samples are presented in Table 3. The data in brackets are semi-quantitative values with relative errors greater than 15% or just

a single measurement. Most of the standard deviations were below 10%. Figures 2 and 3 shows the curve obtained after dividing the concentration of each element with their respective concentration in the upper continental crust of the phanerozoic age—UCC [39].

An enrichment of light and medium rare earth elements can be seen in almost all soil samples related to the UCC (Fig. 2). The characteristic soil samples, ALT1, ALT2, A1.0 and A1.1 showed enrichment in uranium, thorium and

hafnium; the altered diabases, samples A2.0 and A2.1, showed enrichment for the most of the elements, with the exception of Rb, Th, U and Cr. Contrary results were encountered in the clay sample A3.0, that has collected in a bank located a few meters below the diabases samples; it was depleted for almost all the elements, exception to Hf, Rb, Th and U. Ce was not enriched nor depleted in this sample. It is important to remember that this sample was a retransferred, resulting in a mixing of clays from the various sources.

The saprolite A4.1 and the sample A4.3 were enriched with the medium rare earth elements (MREE), Rb, Hf and Ti. It's interesting to note that the sample A4.3 was described as an isoalterite of the schist sample A4.2 during the sample campaign, but they both have not produce the same chemical signature. The normalized profile of sample A4.2 was similar to the altered diabases (A2.0 and A2.1) because of their enrichment in medium rare earth elements, Ti and V (see Fig. 3). Nevertheless A4.2 was enriched of U, in contrast with these alterites. So, the results have showed a general accumulation of the immobile elements

unless the alterite A4.3 has reflected the original chemical composition. This eventual accumulation would be the cause of the large amount of uranium encountered in the saprolite R13, registered in the previous work on rocks of this region [27].

The results for the sediment cores are presented in Table 4, corresponding to the mean value of the analysed slices in each core; the standard deviation gives an idea variation of the elemental concentration along the core. The ratio values, after normalization, with the UCC Condie's data are presented in Fig. 4. A clear enrichment of LREE, Th, U and Hf in the Itingussú (Iting) core may be noted. For the tidal creek core (CN) there was some depletion for almost all elements, exception for Ba, Eu and Rb. This sample is the one of the most influenced by the marine waters, so may presents a major dilution of matrix in both physically as well as chemically. The amount obtained of Th, Sc, Cr, Co, Fe, Ba, Rb, REE and U are in total agreement to the Iting and FL cores when compared with that obtained by Wasserman et al. [18] for non-industrial area of Sepetiba Bay. On the other hand, Amorim

Table 4 Medium values of the concentration of major elements (%) and trace elements (mg kg^{-1}) in the sediment cores and their variation coefficients

|	Iting	SD%	FL	SD%	CN	SD%
Na (%)	1.33	9	1.67	12	1.63	11
Mg (%)	0.976	16	0.684	18	0.893	23
Al (%)	5.68	13	5.552	11	6.23	12
Fe (%)	2.06	18	1.52	18	1.25	59
Ti (%)	0.288	28	0.246	25	0.167	54
Ca (%)	0.934	19	0.990	13	1.06	15
Mn	225	19	187	20	137	52
V	42.7	45	32.8	35	25.8	60
Ba	621	9	650	10	695	15
Cs	3.12	15	2.22	17	2.53	48
La	51.4	43	25.7	26	9.76	30
Ce	106	36	57.2	21	17.0	41
Sm	8.80	34	4.16	24	1.64	27
Eu	1.08	12	0.990	12	0.851	11
Dy	2.84	28	2.56	29	0.949	41
Sc	7.37	18	5.87	15	3.84	47
Cr	27.6	14	23.4	17	17.8	51
Co	6.41	16	4.26	16	4.09	61
Rb	113	8	95.2	10	113	20
Sb	0.804	16	0.749	26	0.952	38
Lu	0.223	35	0.263	29	0.0645	41
Hf	16.7	45	15.9	24	2.34	24
Th	20.6	46	8.53	46	2.01	58
U	6.55	32	6.50	36	1.18	19
Nd	46.6	34	31.2	18	13.0	36
Yb	1.81	32	1.74	33	0.372	41
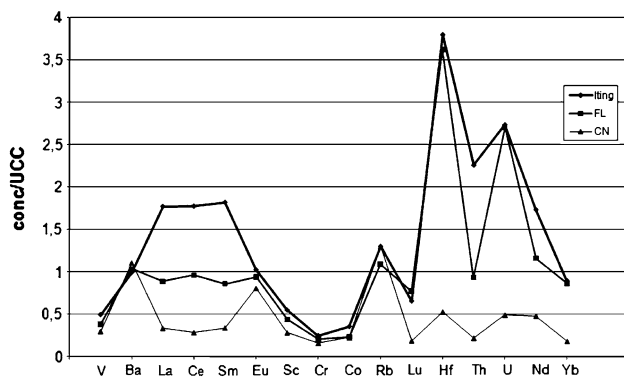
Fig. 4 Normalized values for trace elements in sediment samples

et al. have studied the sediments from Cananeia, a protected environmental area of Cananéia-Iguape estuarine-lagoon complex—Brazil, composed of five water bodies and four islands [40]. Their results were similar to the obtained in this work, exception for the light rare earth elements, which were somewhat greater in the Iting core. The amount of Th and U was greater than the values obtained by Amorim to both Iting and Fl cores too,

pointing out to the contribution of the minerals enriched with these elements to the geological systems of the Sepetiba Bay.

The values encountered in this work to the elements Cr, Mn and Al are below than the values obtained by Silva et al. in the sediments from Cubatão (Cr: 64–72 ppm; Mn: 0.05–0.1% and Al: 8–9.5%) [41]. Cubatão is an important industrial area of Santos Bay, São Paulo, characterized by the occurrence of estuaries and mangrove. So, the minor values for Cr in the Iting cores confirm the minor anthropogenic influence in the Itingussú Bay when compared with a region very impacted like Cubatão. The other hand, the great values for Ca in the Itingussú Bay when compared with obtained to Cubatão (0.3–0.5%) demonstrates the intense influence of marine waters as well as the contribution of apatite, a terrigenous source of Ca, in the Sepetiba Bay [27].

It's interesting to note that the REE concentrations in this tropical ecosystem are greater than these obtained in the sediments of other geographical systems. For example, the Danube River showed elemental values only comparable to the FL core [42]. And in the peat cores from ombrotrophic bogs of Norway, the amount of REE is so

Table 5 Principal components extraction. Critical factor >0.700

Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Na	0.654	0.106	−0.086	**0.712**	0.114
Mg	0.099	0.189	**0.819**	−0.098	−0.013
Al	−0.053	0.349	**−0.920**	−0.124	−0.031
Fe	**0.952**	0.064	−0.014	−0.030	0.276
Ti	**0.959**	0.177	0.161	0.139	0.029
Mn	**0.982**	0.093	−0.034	0.103	−0.113
V	**0.873**	0.258	0.203	0.132	0.079
Ba	−0.455	0.296	−0.609	0.127	0.447
Cs	0.470	0.219	−0.302	−0.577	0.128
Cr	0.330	−0.142	0.181	0.136	0.897
Co	**0.965**	−0.055	0.033	0.084	0.104
Rb	−0.377	0.074	−0.677	−0.512	−0.342
La	−0.028	**0.976**	−0.137	0.112	−0.026
Ce	0.099	**0.982**	−0.055	0.099	−0.097
Nd	−0.122	**0.985**	0.083	0.019	−0.066
Sm	0.419	**0.840**	0.118	−0.094	0.010
Eu	**0.758**	−0.133	−0.445	0.179	0.252
Dy	0.266	**0.867**	−0.016	−0.222	0.252
Sc	**0.943**	−0.084	0.183	−0.115	0.087
Lu	**0.725**	0.069	0.330	−0.457	0.010
Hf	−0.109	0.246	**0.785**	−0.351	0.304
Th	−0.160	0.690	−0.319	−0.530	−0.333
U	−0.0405	−0.036	0.099	**−0.981**	−0.069
Prp. Totl	0.344	0.233	0.159	0.130	0.070

Obs Data matrix includes the values rock samples of the Itingussú region, published in Araripe et al. [27]. The bold coefficients are greater than the critical value 0,7

low that it was low of detection limit of INAA method employed by Fontasyeva e Steinner [43].

Table 5 presents the statistical results for the principal component analysis. It was found a first factor, corresponding to 37% of total variance of data matrix, involving the following elements: Fe, Ti, V, Mn, Sc, Eu, Lu and Co, point out the influence of iron minerals in the geological sample analyzed. The second factor, corresponding to 24% of the total variance, describes a source of La, Ce, Nd, Sm and Dy. It can be related to the presence of allanite, the REE mineral. The third factor contributes with 16% of total variance, and fits to the elements Mg, Hf and Al; the last one has a negative value of significance. The element Rb and Ba have negative values as well, but slightly below the critical value (0.7). This third factor may be pointing to the solubilization of feldspars and formation of clays. The feldspar belongs to the group of aluminum silicates with potassium, sodium, calcium and more rare barium [44, 45].

The fourth factor, with 12% or total variance has a significant factor to Na and higher negative significant factor to U. This seems to confirm the lixiviation of soluble salts with preconcentration of uranium, since the increase of sodium in sediments was not linked with a depletion of uranium.

There were four more components that contribute to the remainder variance. It is possible to hypothesize colloidal transport, organic matter, biological productivity and marine contributions like important influences in the mangrove environment.

The z-score results are presented in a graphic (Fig. 5) for rocks, soil and sediments samples. For the rock samples, most of the elements are in the intermediate position. Almost all elements were more concentrated in the soil when compare to the rocks. The immobile elements clearly show an inverse behaviour in these two types of samples, including the REE. The element Nd was not determined in
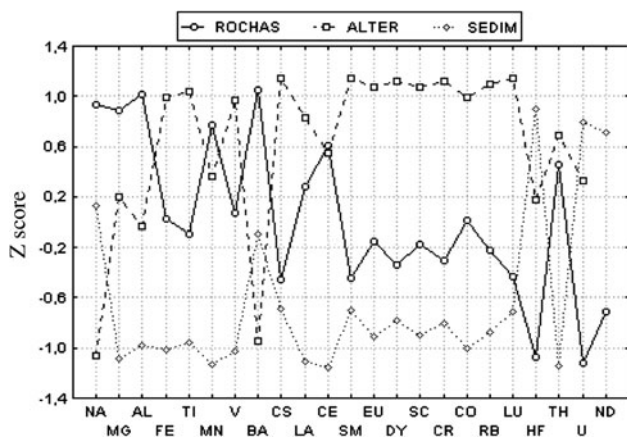
the soil samples, due to the lack of certified material of this element in the Standard Red Clay as used by the authors of this work in the INAA. The sediments of mangrove follow the same signature of the soil in respect of REE. It showed an increase in amount of Na, Ba, Hf and U, but depletion in Th concentration. Hf and U are associated with zircon, so marine influence in the concentrations for this group of elements is not completely clear. The Th depletion can be associated with the physical dilution of matrix during the forming of these sediments when compared with soil or an immobilization of Th by the soil before it arrived in the sediments.

The cluster analysis was applied for all considered samples, including the rocks of the previous work already cited [27], and a dendogram was produced and shown in Fig. 6. The multivariate analysis classified two well separated groups: a minor group includes samples of the maphic dikes, wich contribute little to the chemical composition of the soil. All other samples belong to the more extent group. In the latter it is possible to visualise the lithological influences on the chemical composition of the analysed soils and sediments in the studied area. This major group is composed of an outlier (R2, rock enriched with REE and Th) and two minor subgroups: one of them includes one of the most representatives of the surrounded soil samples (A1.0, A1.1, ALT1 and ALT2) and A4.3. This subgroup has little distance from R2 Although in the another subgroup, the leucocratic rocks R3,R8 and R13 was next R2 either, the entirely ensemble was composed of the sediments of mangrove, and the mesocratic rocks R1, R10, R4, the poorly lixiviated rocks R11, R12, the leucocratic rock R5 and the pegmatite R9. The alterite A4.1 was classified in this group too. The distance of the mesocratic rocks (R1, R10 e R4) suggests that these lithotypes have little influence in the chemical composition of the terrigenous sediments. The same algorithm was employed to log normalized data, without differences in the overall
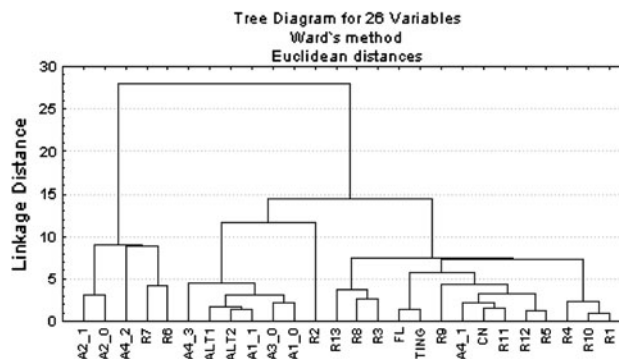

Fig. 5 Dilution graphic depicted with the normalized medium values of the 23 elements obtained in the three types of samples from drainage bay of Itingussú

Fig. 6 Dendogram with all samples—Group G1 includes an samples *A2.1—R6*; The G2 includes samples *A4.3 to R1*. It is composed of two subgroups and an outlier (*R2*), named G2a, that includes samples *A4.3 to A1.0;* and G2b, wich is composed of the poorly samples, *R13 to R1*

scenario, in other words, the type of distribution of the data didn't change the dendogram [46].

Conclusion

A medium soils and sediments composition was obtained of from Itingussú Drainage Bay, as well as its relation with the lithotypes as earlier studied by the authors of this work. The data of soil and mangrove sediments must be considered a reflection of the environmental situation of the beginning of 2000 years. It seems that the anthropogenic impact in the sediments from the west of Sepetiba Bay was still low in this decade, probably due to hydrodynamics factors. Therefore the results of the terrigenous elements measured in this work can be considered reference of the natural chemical composition of the sediments thenceforward.

The zeta score analysis showed the same signature of soil and sediments of mangrove in respect of REE. Nevertheless, it showed a raise in amount of Na, Ba, Hf and U and depletion in Th concentration. Finally, Multivariate Statistical Analysis has clearly indicated that the soil and mangrove sediments formed in this area have been influenced by the leucocratic rocks, which were enriched with light REE.

A great doubt remained in this work is the origin of U to soil and sediments. There were three samples of alterites very enriched with this element. Since the composition of rocks used here hasn't showed any enrichment of U, it's reasonable suggest that an effective mechanism of transport and pre-concentration of this element in the soil. Although the marine origin of U to the sediments still cannot be discharged and it would be necessary radiochemical studies of its isotopic reasons in order to conclude about its origin.

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