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ORIGINAL ARTICLE

Instrumental neutron activation analysis, gamma spectrometry and geographic information system techniques in the determination and mapping of rare earth element in phosphogypsum stacks

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Abstract Phosphogypsum is a by-product from the phosphate fertilizer industry, disposed in huge stacks in open-air storage areas. Its use in agriculture may be a solution to decrease these stacks, because, among its other uses, phosphogypsum can be used as a soil amendment to provide calcium and sulphur for major crops. However, it contains rare earth elements (REE) from its raw material. The objective of this study was to determine the concentrations of REE in phosphogypsum stacks Imbituba (southern Brazil) in order to verify the possibility of contamination in the surrounding of the stacks due to the disposal and to ensure the safe use of phosphogypsum in agriculture. Samples of phosphogypsum were collected and REE were determined by neutron activation analysis and gamma spectrometry. There was no leaching of the REE through the profile of the stacks, which suggests that the occurrence of REE in the phosphogypsum is associated with the formation of sulphates, carbonates, fluorides and phosphates. The results indicate that application of phosphogypsum from Imbituba to agricultural soils can contribute to increase the concentration of rare earth elements in the cultivated soils, but these are not available to plant uptake.

Keywords Rare earth elements · Instrumental neutron activation analysis · Phosphogypsum · Soil pollution

Introduction

The use of fertilizers and soil amendments is crucial for enhancing agricultural production in soils that have been impoverished due to intensive farming cycles. However, concerns about the pollution caused by the agricultural use of such materials have grown, and the identification and characterization of sources of contamination are critical needs for the establishment and maintenance of public policies for controlling, supervising and regulating agricultural activities (Le Bourlegat 2010).

Among the materials used as soil amendment is the phosphogypsum, a by-product of phosphate fertilizer industry, likely represents a valid solution. Studies aimed to evaluate the possible uses of phosphogypsum have become increasingly important from an economic, technological and an environmental point of view, since it is abundant and has low cost waste thus avoiding commitment of the areas where this material is stockpiled. Furthermore, its use would contribute for the preservation of natural gypsum reserves, thus ensuring a basic principle of sustainable development, namely the preservation of natural resources for future generations (Oliveira 2012).

The phosphate industry uses phosphate rocks as raw material for the phosphoric acid and phosphogypsum by-product production. The phosphate rocks deposit can be of igneous or sedimentary origin. The igneous deposits are

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responsible for 15–20 % of the worldwide production and the sedimentary deposits for 80 to 85 % (Lima 1989).

The phosphate rocks represent a small part of the world resource (about 1 %) and are in the range of about 300 million tons of ore (Departamento Nacional de Produção Mineral (DNPM) 1993). They are distributed by many states, but are mainly concentrated in Minas Gerais, São Paulo and Goiás. In addition to this reserve, Brazil imports natural phosphate ore from several countries, such as United States, Israel, Morrocco and Tunisia. About 80 % of the Brazilian reserves are of igneous type, they are predominately exploited in Araxá (southeast Brazil), Catalão (Midwest Brazil) and Jacupiranga (southeast Brazil), apatite being the main component of the national phosphate rocks. As far as the sedimentary deposits are concerned, the locations are in the northeast states, especially Pernambuco and Patos de Minas (MG), being able to contrast the main component being the phosphorite.

Although phosphogypsum is mainly composed of dehydrated calcium sulphate, whose chemical and physical characteristics are similar to natural gypsum, it can contain high levels of impurities, as metals, radionuclides and rare earth elements (REE) from the phosphate rock matrix (Fernandes et al. 2004). Phosphogypsum has been used for decades as an agricultural input, mainly in the Brazilian Midwest region, considered as the agricultural frontier in Brazil, where its use is of extreme importance to increase the crop productivity (Souza et al. 1992).

Given the Rare Earth Elements existence in the phosphogypsum used in the agriculture, it becomes necessary to understand the mobility of these elements in the environment and, with that, it is necessary to evaluate whether the use of the phosphogypsum in the soil can ultimately contribute to the raise in human exposition to these elements through the food chain. It is worth mentioning that the Brazilian phosphogypsum appears from the chemical processing of igneous ores and that a big part of the references about the subject-matter are from studies developed in tempered weather countries and with the use of chemical processing of sedimentary phosphogypsum ores, which can raise in uncertainty and hence in risks to which the individuals and/or population which resides in tropical weather are exposed. The number of data available that refers to the culture in tropical regions still are too few, thus, the way to obtain a consistent database in the parameters of transference determined in tropical region is of extreme relevance.

REE can enter the human body through ingestion of contaminated food and by inhalation of airborne particles in suspension. Most ingested rare earths are excreted, however, a small amount may enter the bloodstream through ionic exchange processes and accumulate in various parts of the body (Koeberl and Bayer 1992). Several diseases have been associated with exposure to REE (Sabbioni et al. 1982), but little is known about the effect of these elements in the biosphere because there are few sufficiently sensitive analytical techniques for the determination of REE in air, water, soil and sediments (Chua 1998).

In the Brazilian state of Santa Catarina there are two stacks of phosphogypsum in the Imbituba county. This material is currently marketed and applied in apple and soybean crops. Some studies indicate that the use of this phosphogypsum in agriculture is viable from the radiological point of view (Borges 2011). However, there are no studies regarding the availability of the REE in this material.

In the case of high concentrations of REE in the Imbituba-SC phosphogypsum, we can suggest the use of this by-product to the REE extraction industry, since there is a high worldwide demand because of their wide use in the high technology industries (Embso et al. 2015).

This study aimed to quantify the presence of REE in both stacks of phosphogypsum from Imbituba, infer about their special distribution, leaching to deeper layers and to the surrounding areas and evaluate the safe application of phosphogypsum as a soil amendment in relation to contamination of agricultural soils by REE.

Experimental

Study area

The city of Imbituba is situated on the south coast of Santa Catarina state, 90 km from the capital Florianópolis. The average altitude is of 30 m above sea level. The county locates itself in the coordinates 28°13′17″S and 48°38′21″W, with an area of 184,787 km^2, limited by the Garopaba county in the north, to the south by Laguna county, to the east by Atlantic Ocean and by Imaruí county in the west.

The climate in the region is defined as subtropical and rainy (Mendonça 2007), depending on the situation the interaction of the intertropical and polar masses of air conjunction defines the mesothermic characteristics. Due to its low altitude the summer is hot and lingering. The average temperature in the winter is of 17 °C and in the summer of 25 °C.

The concentration and lixiviation studies of REE were done in two phosphogypsum stacks, which already existed in Imbituba County.

There are two phosphogypsum stacks, a newer one, denominated Stack 1 separated by about 3 km of the company and another one on the limits of the industry, denominated Stack 2, in which both are out of operation since the 90 s. The area is occupied by the oldest deposit (stack 2) is of about 70,000 m^2 and 10 m in height. The most recent one (stack 1) has an area of about 460,000 m^2 and 30 m in height.

The sampling was made in nine georeferenced points in stack 1 and 8 points in stack 2 (Fig. 1), these samples were taken in depths of 0–2 m as a attempt to evaluate the distribution of the REE between the depths of the Stacks.

Georeferenced Samples of the phosphogypsum soil were also taken, next to Stack 2, identified as Praia do Porto (PP) soil and a sediment of the Lagoa de Decantação (LD), in order to verify the contribution of the phosphogypsum to the distribution of REE. Moreover, georeferenced samples were collected in the referenced area (AR), as comparative purposes related to the chemical composition of the local soil without human interference.

The phosphogypsum and soil were taken according to Brazilian laws (ABNT 1987).

In the laboratory, all samples were identified, dried in oven at 40 °C until reaching constant weight and then, right after that, the dried samples were pulverized using an agate mortar to obtain a thin powder.

Spatial analysis

To perform the physical characterization of the phosphogypsum stacks the GIS ArcMap 10 software (ESRI Inc.) was used, which allows managing georeferenced data and performing spatial analysis with digital cartographic databases in vector shapefile format (.shp). In addition to the monitoring data, vector data were stored from the city of Imbituba provided by Google Earth. In order to estimate the levels of REE based on the chemical parameters, the Inverse Distance Weight (IDW) interpolator was adopted. The operating procedures were based on the acquisition, storage, manipulation, analysis and presentation of georeferenced data. The first step constitutes the creation of a database project, identification of the appropriate map projection for the study area.

The IDW works with the hypothesis in which the closest points to be measured are more alike with those which are farthest. Therefore, the IDW interpolation method is a spatial analysis tool which assumes that each of the samples has a local influence which decreases with length. To

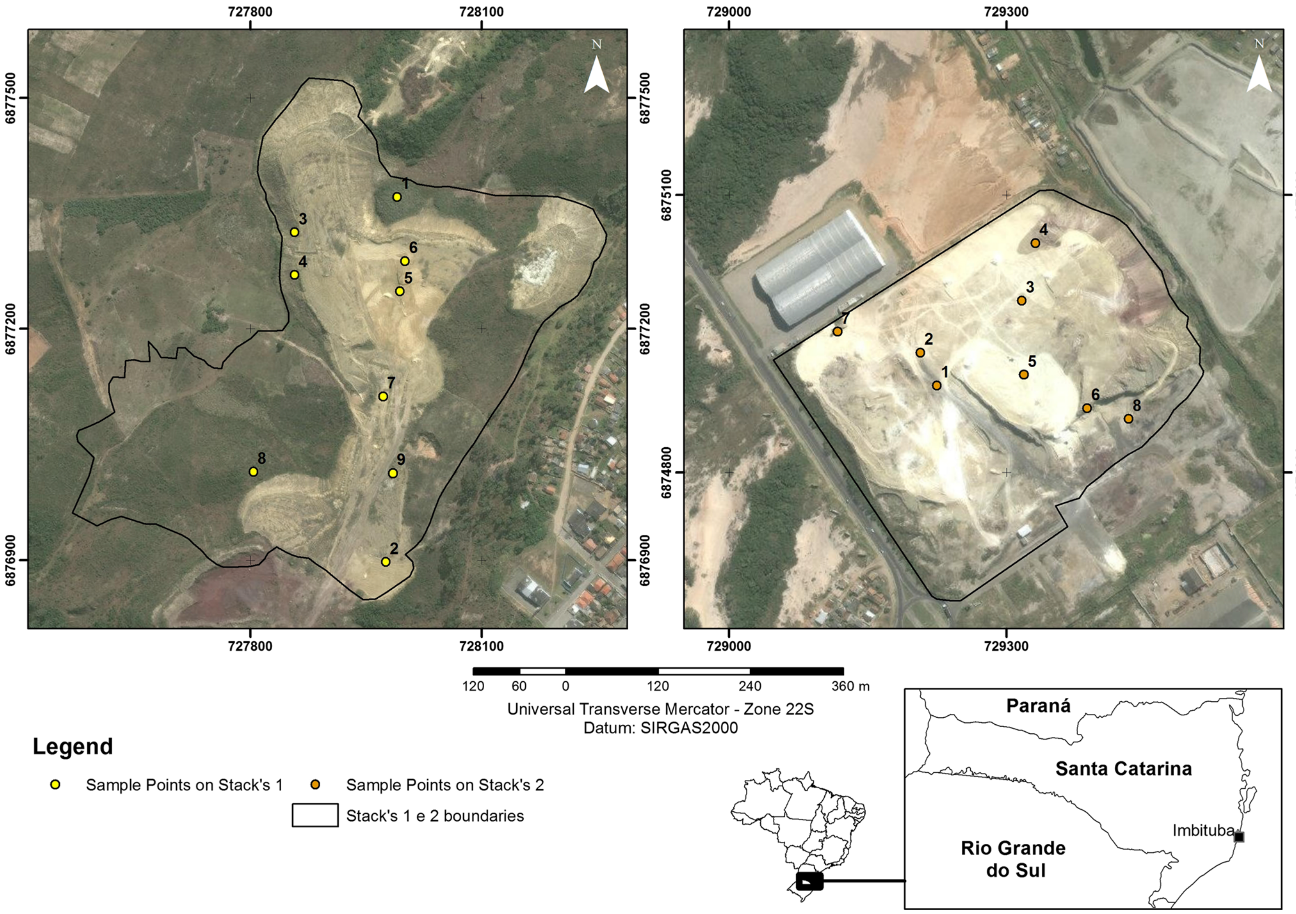

Fig. 1 Sampling point locations for Stack I and II

foresee a value of any place not measured, the IDW uses the values of the neighbor points. Moreover, the closest measured values for the prediction point have more influence over a predicted value of those which are farthest. With this interpolator it is possible to attribute weighs from 0 to 3. The proportional weights are the opposite from the distance (between the samples and the prediction points) to the power of the amount of the p potency. As a result, as the distance increases, the weight decreases rapidly. The decrease rate depends on the p value. If $p = 0$, there is no decrease in distance, and because the weight is the same, the predicament is going to be the average of all the samples given in the search neighbourhood. When p rises, the weight of the distant samples decreases faster. If p value is very high, only the surrounding points will influence the prediction immediately (ESRI 2011).

The inverse distance weighted (IDW) is available in the software ArcGIS 10. This interpolation technique assumes the logic that the variable in which it is being mapped has its influence lowered according to the local sampling distance (Environmental Systems Research Institute—ESRI 2011). The mathematical method adopted by the IDW interpolator is represented in Eq. 1, where: $z =$ interpolated value; $n =$ number of observed individuals; $z_i =$ attributed values to the observed individuals; $d_i =$ distance between the observed individuals and the interpolated one (Varella and Junior 2008).

$$X = \frac{\sum_{i=1}^{n} \frac{1}{d_i^p} Z_i}{\sum_{i=1}^{n} \frac{1}{d_i^p}}. \tag{1}$$

Normally $P = 2$ is used as a standard value, although there isn't any theory to explain the chosen value over the other, and the p value modification should be researched. The outcome is a raster map which is possible to define the pixel size. In this work the pixel matching 10 was considered, due to the scale used. Thus, a verification of the results was conducted with the interpolation of several p values. The p value was chosen through the closest result between the generated pixel and the sample matching such pixel. The assumed value to the potency equals 2.

Instrumental neutron activation analysis and gamma spectrometry procedures

Neutron activation analysis (NAA) is frequently used to obtain data for REE from geological materials (El-Taher 2010). Among the analytical methods for determination of REE, the neutron activation followed by gamma spectrometry with high purity germanium detectors (HPGe) has been highlighted due to the low detection limits, for being a non-destructive technique and the capability of detection of many elements with high sensibility. Also, the method of activation analysis meets two basic requirements of technical non-destructive analysis: the specificity, which is the ability to correlate directly and unambiguously the signal obtained of the sought element, and the selectivity, which is the ability to measure the element in question in the presence of other elements that emit same type signals (Bode et al. 1990).

For the neutron activation analysis about 200 mg samples of phosphogypsum and soil were weighted in polyethylene using a analytical weighing machine with four decimal points. Following that, the capsules were sealed with iron solder with graphite tip.

The standards used were: Podmore Red Clay (Bellido 1988), Phosphate Rock (NIST 694) and San Joaquin Soil (NIST 2709) the standards were prepared in the same way as the samples. The elements determined by INAA were La, Ce, Sm, Eu, Dy and Yb.

Elements of long half-life were determined. In this step, the polyethylene capsules with the samples, blanks and standards were made using proper aluminium can storage to be irradiated for a longer time. In each aluminium recipient there were six samples, one blank and three standards distributed in homogeneous form. The characteristics to this irradiation were:

Irradiation time: 4 h.
Decay time: 10 h.
Time to count: 2 h.

The encapsulated samples, blanks and standards were submitted to a thermo neutron flux of about 10^{13} n cm^{-2} s^{-1} in the research reactor IEA-R1 of the Nuclear and Energetic research institute—IPEN/CNEN.

With the decay time over, the samples, blanks and standards were counted by a hyper pure germanium with electronic associated of Ortec type Inc. (45 % efficiency with for 4096 channels resolution) in the radiochemical laboratory at Universidade Federal Fluminense.

The detector calibration was made through the relation Energy × Channel, with calibration sources of ^{152}Eu and of ^{60}Co made by Amersham, with the objective to maintain the quality control of the samples, it was also made a background check and efficiency curve. The spectrum accumulation was made using the RAE program (Bellido 1988) associated to the Maestro program developed by Ortec Inc.

Statistical analysis

The multivariate statistical methods were used with the objective of identifying the human contamination, however, for that it must be considered the high complexity presented by the environmental studies (Einax and Soldt 1999). Group samples were realized to determine which parameters contributed the most to the characterization of the evaluated material. The program used in the statistical analysis was STATISTICA 7 (Starsoft Inc.).

Results and discussion

The REE in phosphogypsum are derived by its raw material (phosphate rocks). Basically there are two kinds of phosphate rocks: the sedimentary (88 % of the world total, occurring in North Africa, Tunisia, Saudi Arabia and, United States among others) and igneous rock, occurring in Russia, South Africa and Brazil (Sabiha-Javied et al. 2008). Igneous phosphates contain thorium and REE related, while sedimentary rocks shows more uranium (Bragança et al. 2003; Menzel 1968; Rutherford et al. 1994).

Igneous Phosphates have Thorium and Rare Earth associated, on the other hand the ones of sedimentary origin have more Uranium (Bragança et al. 2003). The REE source of phosphogypsum is from the ore matrix used on the phosphoric acid process of production. As mentioned before in the subject-matter study, the phosphogypsum generated in Imbituba-SC phosphate rocks were formed from multiple origins; stack 1 formed by igneous phosphate ores that came from Araxá-MG and the stack 2 formed in its majority by phosphate sedimentary ores imported from Florida and Morocco. Therefore, the REE concentration can be very different in each studied stack.

The phosphogypsum analyzed in this study showed a concentration of REE similar to those cited in the literature (Table 1), except for Dy and La which had concentrations above and below the ones cited by other authors, respectively.

The total concentration of REE in the phosphogypsum was 1432 mg kg^{-1} in stack 1 and 330.5 mg kg^{-1} at stack 2. The ratios of the La/Yb were 6.6 for the stack 1 and 0.13 for the stack 2.

The phosphogypsum evaluated in two stacks showed notable differences, due to the kind of phosphate rock (igneous or sedimentary). The REE can be used as tools in the study to differentiate the source of each rock types.

Turra et al. (2011) have found values of REE concentration in samples of some agricultural inputs such as calcium nitrate (approximately 6 mg kg^{-1}), magnesium sulphate (about 4 mg kg^{-1}), magnesium nitrate (on the order of 3 mg kg^{-1}), monoammonium phosphate (MAP) (10 mg kg^{-1}), superphosphate (3000 mg kg^{-1}) and also in NPK fertilizers (varying between 1000 mg kg^{-1} and 2000 mg kg^{-1}) and thermophosphates (of the order of 3251 mg kg^{-1}).

Considering that the average dose recommended for applying thermophosphate in soil ranges from 300 to 1500 kg ha^{-1} (Mitsui Fertilizer Company 2006), the total amount of REE applied can vary between 1 and 5 kg ha^{-1}. The recommended dose or application of phosphogypsum in sandy soils is approximately 990 kg ha^{-1} and in clay soils is 4400 kg ha^{-1} with an interval of 4 years (Souza et al. 1992), the total amount of REE (Table 2) which would be applied ranges from 3.6 to 17.6 kg ha^{-1} for sandy and clay soils, respectively (Oliveira 2012).

Figure 2 presents the results for Lanthanum (La). La has a great affinity for F and P which manifests on a large variety of minerals occurring in granites, pegmatites and mainly apatite. The global average in the Earth's crust is 43 mg kg^{-1} (Kabata-Pendias and Pendias 1992). The contents of La in stack 1 samples are considered intermediate when compared to the values determined for igneous rocks and are below the global average. In stack 1, the average concentration of La was 27.2 mg kg^{-1} but the maximum concentration reached 42 mg kg^{-1}. The first depth (0–40 cm) showed more samples with this maximum concentration.

Few samples of phosphogypsum collected in the second and third depth of the first stack showed the maximum concentration for La. Thus it can be concluded that there was no leaching of this REE through the stack 1.

The average concentration of La found in stack 2 was 24.1 mg kg^{-1}, lower than the ones mentioned above in the

Table 1 Concentration (mean ± standard deviation mg kg^{-1}) of rare earth elements from phosphogypsum in samples from different sources

Element	Rússia[a]	Brazil[b]	Brazil[c]	Brazil[d]	Stack 1	Stack 2
La	1050	1300	1017	973	27.2 ± 4	24.1 ± 4
Ce	1600	2574	956	1730	1232.9 ± 326	25.3 ± 251
Sm	76	149	123	85	70.4 ± 12	32.1 ± 8
Eu	30.4	36	26	29	35.8 ± 3	29.6 ± 3
Dy	–	–	–	8	61.5 ± 13	31.9 ± 7
Yb	3.9	4.3	10	5	4.1 ± 1	187.5 ± 113

[a] Gorbunov et al. 1992

[b] Santos et al. 2006

[c] Le Bourlegat 2010

[d] Oliveira 2012

Table 2 Increment of rare earths in soils treated with agricultural inputs

Agricultural input	Dose (kg ha^{-1})	REE total (kg ha^{-1})
Thermophosphate	300–1500	1–5
NPK	100–400	0.14–0.58
Phosphogypsum	990–4400	3.6–17.6

Oliveira 2012

literature. In the second depth was observed the highest concentration of this element, with some points showing concentration over the average in this depth, reaching 190.44 mg kg^{-1}. This result suggests that the leaching of this element was not observed within the stack 2.

Embso et al. (2015), said that when studying the REE in phosphate ores of the USA, La concentration found had values in the range of 37.15–2718 mg kg^{-1}. While Ihlen

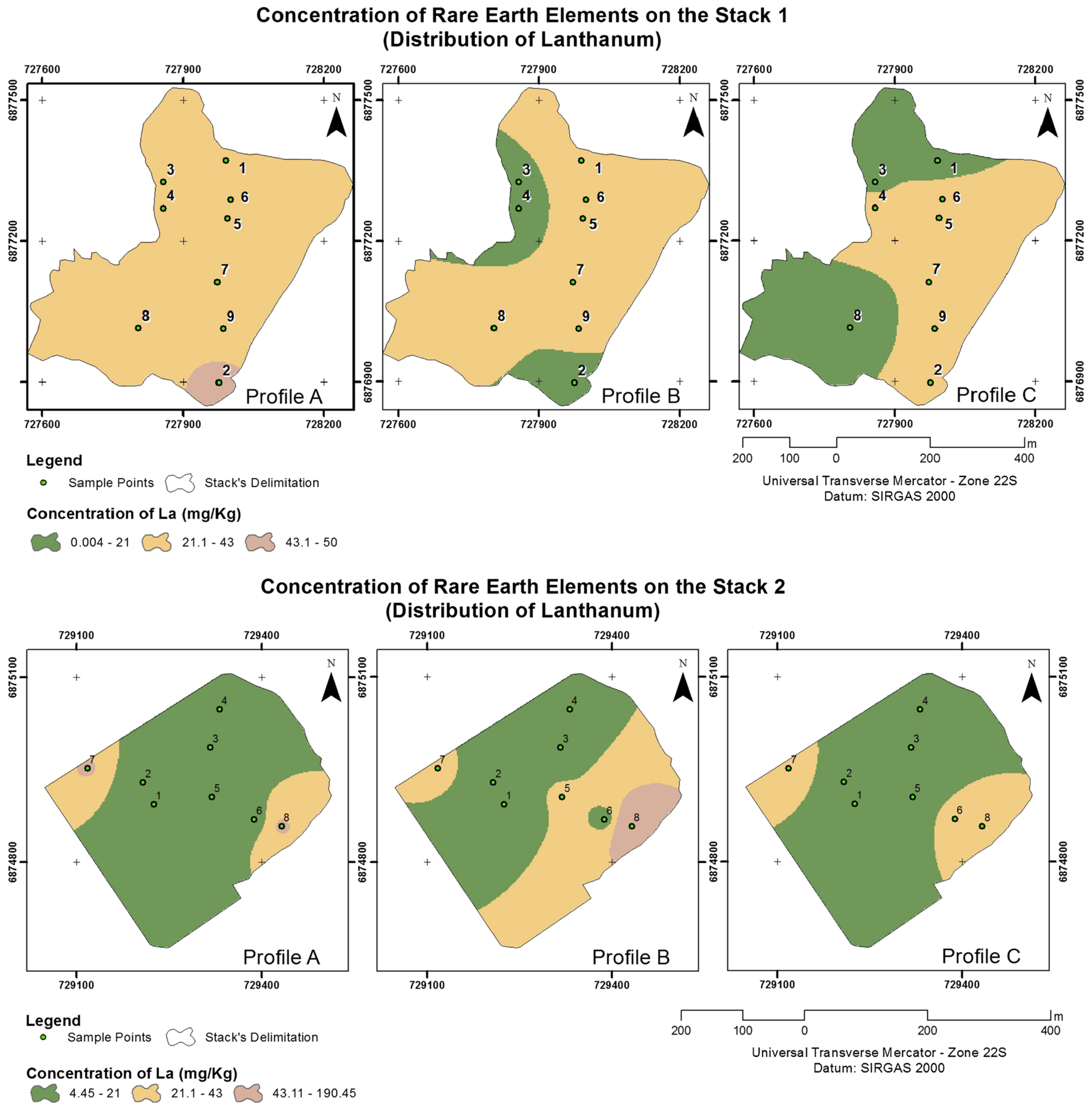

Fig. 2 Distribution of lanthanum with depth in phosphogypsum stack 1 and stack 2, respectively

et al. (2014), said that studying REE in Norwegian igneous phosphate ores, La concentration values found were in the range of 164.5–2456.5 mg kg^{-1}.

The Fig. 3 shows the distribution of REE with the depth in phosphogypsum stack 1 and 2. In the Earth crust, the average concentration of Ce is 66 mg kg^{-1}. The maximum allowable concentration for Ce in Dutch soils is 53 mg kg^{-1} (Sneller et al. 2000). There are no established guideline values for this element in Brazil. However, in this work, stack 1 had Ce values 1232.9 mg kg^{-1} which were much higher than the allowed by Dutch legislation, which may hinder the use of the waste in agriculture. It can be noted that there was no leaching of this element through stack 1. Comparing between the values of Ce in igneous phosphate ores (Ihlen et al. 2014), the concentration in stack 1 is in the range for the apatite in Norway 494.4–5352.9 mg kg^{-1}, which confirms, again, the high concentration of REE in igneous rocks.

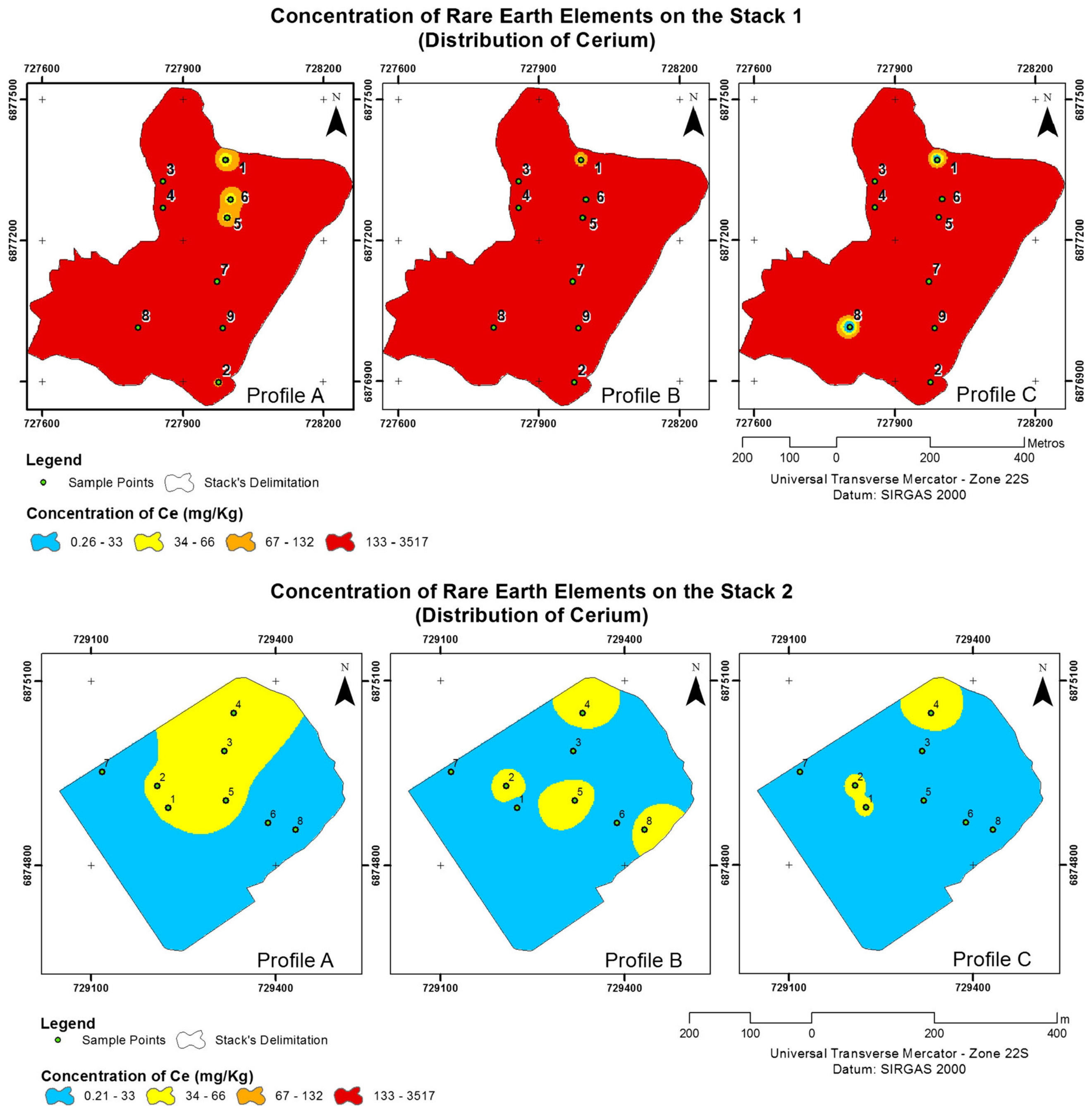

Fig. 3 Distribution of cerium with depth in phosphogypsum stack 1 and stack 2, respectively

However, the average value of Ce in stack 2 was under this limit (25 mg kg^{-1}). Otherwise, the maximum concentration found in stack 2 was 49.85 mg kg^{-1}, and can be noted that, in the three depths, the majority of samples showed Ce concentration near the maximum levels found. These results corroborate with the values found by Embso et al. 2015, which states that phosphate rocks of sedimentary origin have Ce in the range of 52.11–253.85 mg kg^{-1}, showing the lowest values of Ce in these kinds of rocks.

When comparing the two stacks we can observe that the stack 1 has much higher Ce concentrations than stack 2, probably because this fact is associated to the types of phosphate rocks in which the piles were originated. Stack 1 was formed only by phosphate rocks of igneous origin from Araxá, that being the rocks rich in light REE like Ce, while stack 2 was formed by phosphate rocks of sedimentary origin from Florida and Morocco.

Figure 4 presents the results for Samarium (Sm) for both stacks. The average found in stack 1 of phosphogypsum was 70 mg kg^{-1}, less than those cited in the literature, for instance, Ihlen et al. 2014, which has found concentrations of Sm in igneous phosphate rocks in the range of 86.3–323.3 mg kg^{-1}. This fact is probably associated with the redistribution of these elements that have suffered from the chemical processing of phosphate rock. Observing the concentration through the depth, no leaching was noted: the surface samples presented the highest concentration of this REE and samples from the third depth showed the lowest level, demonstrating that the leaching did not occur.

The average concentration found for Sm in stack 2 was 34 mg kg^{-1}, which is in the range with the value mentioned in the literature for phosphate rocks of sedimentary origin 18.91–32.90 mg kg^{-1} (Embso et al. 2015). This fact is probably associated with the redistribution of this element from the chemical processing of phosphate rock. To Sm, the samples collected in the surface showed the highest concentration, reaching 58.06 mg kg^{-1}. Again, there was no leaching of this element to stack 2.

Comparing both stacks, it can be observed that the stack 1 presents much higher concentrations of Sm in all depths compared to stack 2, this fact is probably due to the different kind of phosphate rocks which originated each stack.

In Fig. 5 can be seen the results for Europium (Eu). Its abundance in the Earth's crust is about 2.14 mg kg^{-1} (Fortescue 1992). The global average concentration in soils is 0.85 mg kg^{-1} (Kabata-Pendias and Pendias 1992). The mean value obtained in stack 1 was 35 mg kg^{-1}, higher than those determined for the crust and soil, but still in range of the concentrations found in igneous phosphate rocks 21.5–73.7 (Ihlen et al. 2014). This can be explained due the loss of the secular equilibrium during its chemical processing. This way, the impurities were redistributed between the waste and the phosphoric acid. It is verified that Eu was found in high concentrations on the majority of the sampling points of the stack 1, in all depth evaluated.

The average values of Eu were 29.6 mg kg^{-1} in stack 2 and were above the value determined by Tyler (2004) for Earth crust (2.1 mg kg^{-1}). The behaviour and concentration of this element in the two stacks studied were similar. Samples collected on the second depth presented the highest concentrations of this REE, reaching 39 mg kg^{-1}, highly different from the values found for the sedimentary phosphate rocks which varies from 2350–2975 mg kg^{-1} (Embso et al. 2015).

The dysprosium (Dy) behaviour is showed in Fig. 6. It can be observed that there was a variation from 39.48 to 97.35 mg kg^{-1}, and the samples collected in the surface showed the higher concentration for the element, this way it can be stated there was no leaching through the depth also, in the stack 1. These Concentrations corroborate with the range found on the igneous phosphate rocks 46–140.9 mg kg^{-1} (Ihlen et al. 2014).

This REE, the highest concentration was found in the surface samples, followed by the third depth in stack 2, fact that corroborate with the conclusion that no leaching of Dy occurred. Showing 31.9 mg kg^{-1} the average concentration for stack 2. This means that the concentration of this stack is within range of the sedimentary phosphate rocks 38–70 mg kg^{-1} (Embso et al. 2015).

Stack 1 presents concentrations of Dy above stack 2, which the biggest concentration found was of 51.48 mg kg^{-1}, while in stack 1 the biggest concentration found was of 97.5 mg kg^{-1}, which means it is almost double the concentration of Dy. These results probably are associated to the kind of phosphate ore which each was taken from.

The results for ytterbium (Yb) are presented in Fig. 7. In stack 1 the values of this element 1.62–9.82 mg kg^{-1} remained below the cited in the literature, (Ihlen et al. 2014), studied the phosphate rocks of igneous origin in Norway and found the concentration of Yb 8.8–43.6 mg kg^{-1}.

The surface samples in stack 2 showed the highest concentration of Yb, reaching the maximum value of 838 mg kg^{-1}. The variation of this element in the samples and in the different depths varied largely: 1.84–838 mg kg^{-1}. In phosphate rocks of sedimentary origin the concentration of Yb varies from 2–9442 mg kg^{-1} (Embso et al. 2015), these results show that the values found on stack 2 are in the expected range for sedimentary rocks.

The concentrations of Yb were the ones which presents the highest variation between the stacks, being that a difference of 1–2 in magnitude order. In stack 1 the biggest concentration was of 9.82 mg kg^{-1}, while stack 2 reaches values of 838.68 mg^{-1}. The high concentration found in

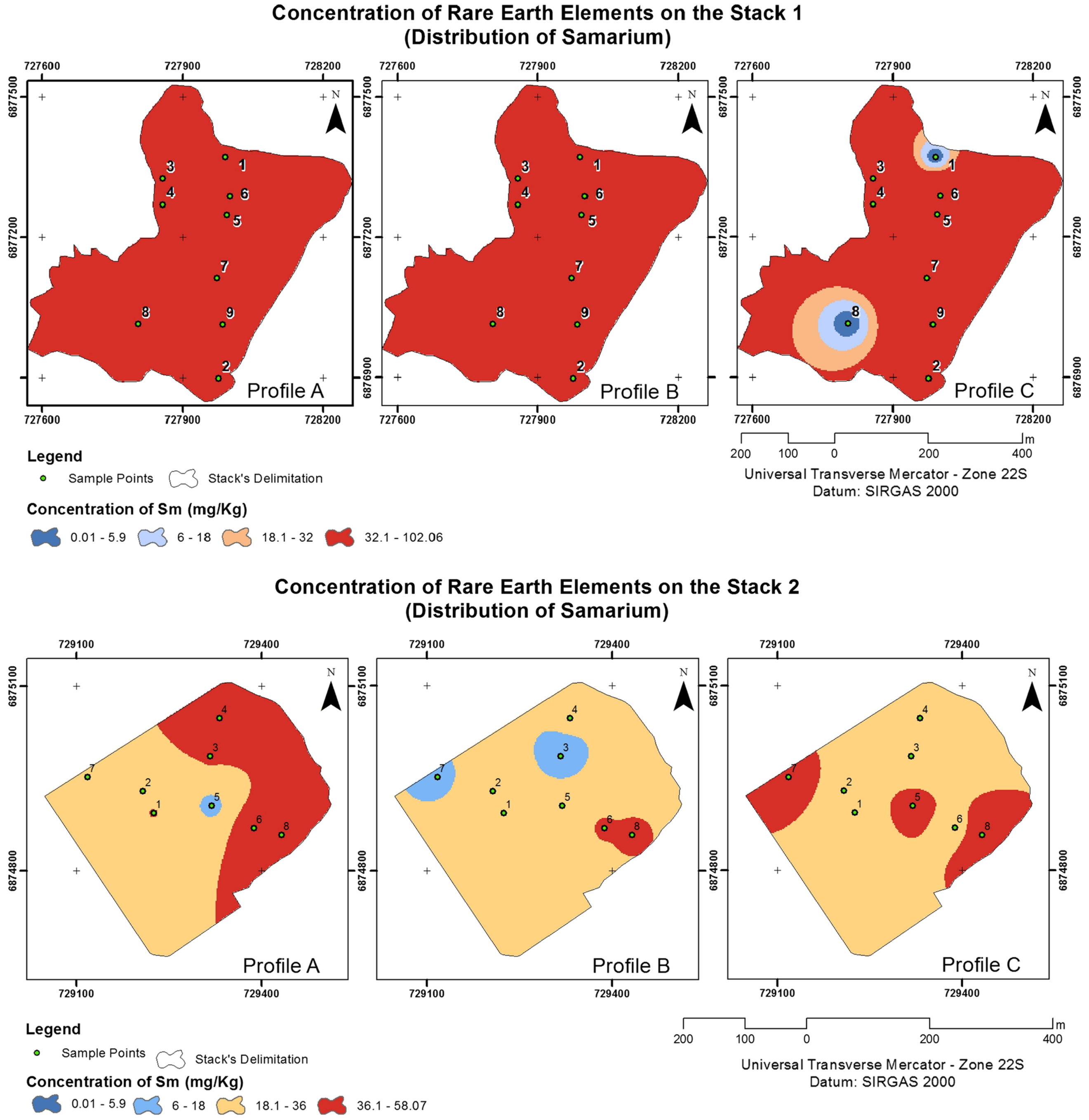

Fig. 4 Distribution of samarium with depth in phosphogypsum stack 1 and stack 2, respectively

stack 2 can be associated to the sedimentary phosphate rocks which it was originated from Florida and Morocco.

It can be observed that the evaluated REE showed small variation with the depths, except for Ce which in some points varied widely. The lack of similarity in the distribution of these elements with depth suggests that the chemical composition of the phosphogypsum depends on the nature of the phosphate minerals and the digestion process.

Figure 8 presents the REE concentrations were normalized to the chondrite CI (Sun and McDonough, 1989).

The analyzed phosphogypsum in stack 2 is imported from Morocco and Florida, originated from the phosphorite processing. While the phosphogypsum analyzed in stack 1 is originated from apatite processing, derived of phosphorous ore from national origin. The geological origin of the processed rocks and the mineral association explains the different concentrations of the rare earth elements in the

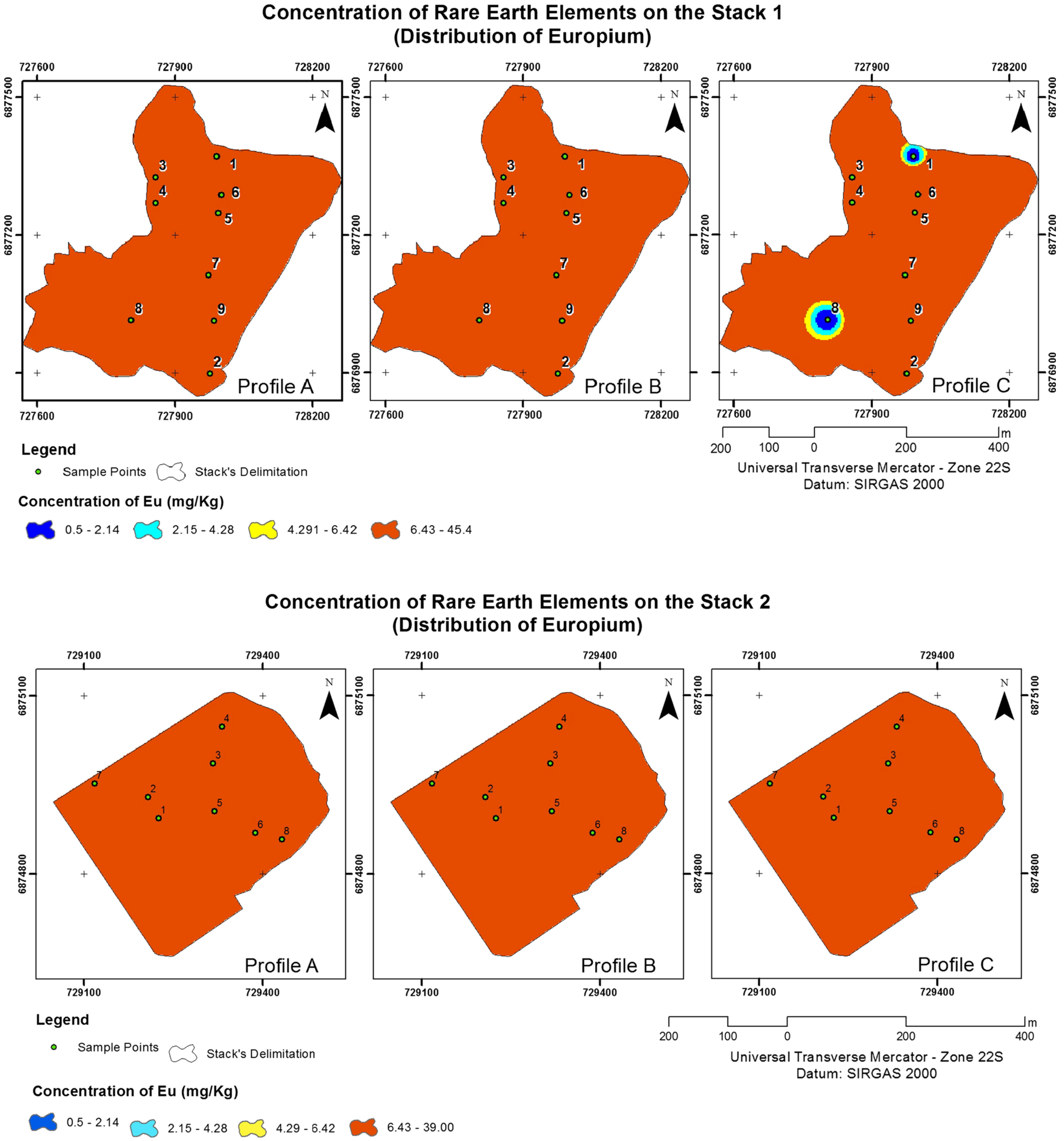

Fig. 5 Distribution of europium with depth in phosphogypsum stack 1 and stack 2, respectively

Brazilian phosphogypsum, when compared to the international results.

The apatite, together with its varieties, creates an important mineral group, where the Ca^{2+} can be replaced, partially, by positive ions such as: ETR, Cerium mainly in the igneous apatite and Cerium-Yttrium in the sedimentary origin. These data corroborate with the results obtained in the normalization of the phosphogypsum stacks once the stack 2 of sedimentary origin presented itself enriched with Ce and Yb.

In general, phosphate minerals are the ones which provide the most contribution for the REEs supply in the soil, which is directly related to its mineral genesis (Picard 2002). The phosphatized rock is used in the production of

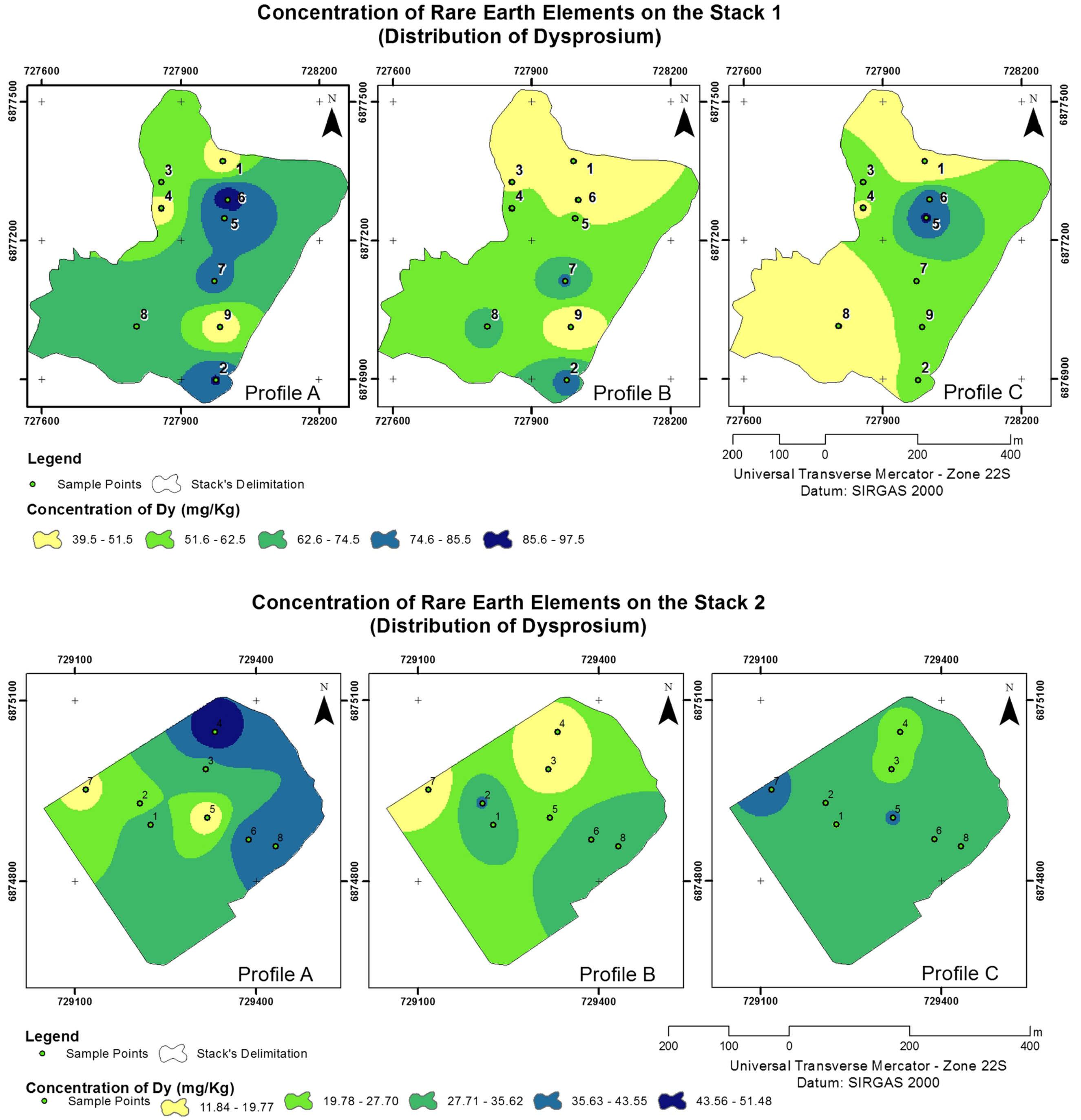

Fig. 6 Distribution of dysprosium with depth in phosphogypsum stack 1 and stack 2, respectively

many fertilizers, beyond just phosphoric acid, and they can contain or not high solubility in water and P_2O_5 ratio which is requested on the fabrication process.

The phosphate fertilizer production in Brazil is due exclusively by a sulphuric route (Lapido-Loureiro 2008; Melamed and Neto 2008). The sulphuric route is considered cheaper. However, generates a big quantity of phosphogypsum, its by-product, which its composition is mainly of calcium sulphate.

For more clear normalization results, the phosphogypsum stacks in this work were evaluated and compared with other Brazilian and Russian phosphogypsum stacks. It can be noted that stack 1 has a similar signature with the other phosphogypsum stacks from Brazil and Russia for most elements, with the exception of La which presents lower concentrations. Showing that the material in which these stacks were formed is similar.

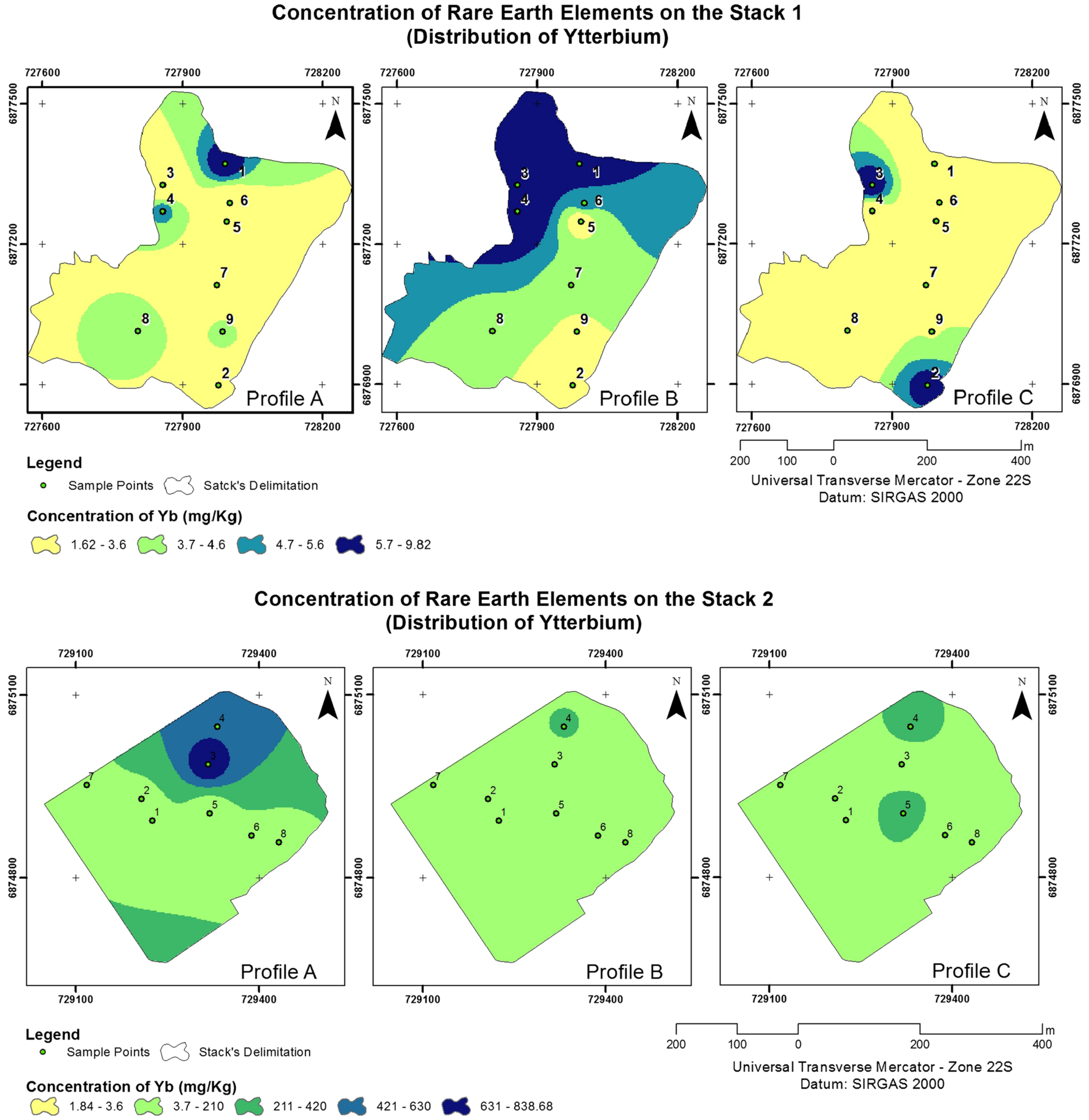

Fig. 7 Distribution of ytterbium with depth in phosphogypsum stack 1 and stack 2, respectively

On the other hand, stack 2 present a totally different signature from the other studied phosphogypsum samples, Eu being the only exception presenting similar concentrations. This fact is probably due to the original material have a chemical composition that is very different from the other phosphogypsum samples and is associated mainly to the different kind of sedimentary rocks from Florida and Morocco, which were used in its formation.

The occurrence of REE in the phosphogypsum is associated with the formation of complexes with the anions sulphates, carbonates, fluorides and but rarely phosphates. According to Lapido-Loureiro (2008) the apatite form an important group of minerals, where Ca^{2+} can be substituted by REE, mainly light REE in igneous rocks, and by heavy and light REE in sedimentary rocks. The results confirm these data, once the stack 1 is formed by igneous rocks and are enriched in La, Ce, Sm and Eu (light REE).

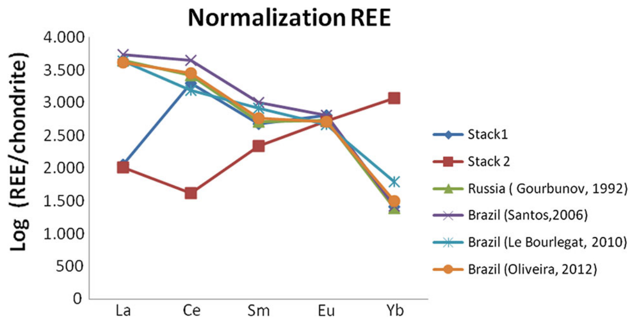

Fig. 8 Chondrite normalization LOG (REE/chondrite). (Sun and McDonough 1989)

Taking into account that the probability of groundwater contamination due to leaching of the REE and that their mobility in the phosphogypsum is relatively low (Hu et al. 2006; Kabata-Pendias and Mukherjee 2007), the continuous application of phosphogypsum, as well as fertilizers could lead to an accumulation of REE in soils agricultural soils. Therefore, in this case, the possible occurrence of deleterious effects to plants and the environment must be considered.

It is interesting to note that the concentration of REE in phosphogypsum samples suggests that these elements may be used as a signature of the phosphogypsum (Santos et al. 2006; Saueia et al. 2005).

There are too few works on literature about REE in phosphogypsum. However, the industries have concentrated in creating mechanisms to recover these elements from the phosphogypsum to use them in other applications (Lokshin et al. 2005; Lokshin et al. 2002; Lebedev and Lokshin 1999; Valkov and Valkov 1996).

The results obtained by the assessment on the influence of the phosphogypsum stacks to the surrounding soils are presented in Table 3 with other results from the literature.

The results of concentration of REE in samples of RA soil were below the cited in the literature for the Earth´s crust (Tyler 2004), except for the elements Eu and Dy that presented concentrations above these values. The soil PP and sediment LD that are nearby the stacks showed for all REE concentrations lower than the ones cited for the Earth's crust (Tyler 2004).

The total concentration of REE was approximately 56.95 mg kg^{-1} in the RA soil (25 times smaller than the concentration in phosphogypsum from stack 1 and 5 times smaller than concentration in phosphogypsum from stack 2) and 33.61 mg kg^{-1} in the soil PP (42 times smaller than the concentration in phosphogypsum from stack 1 and 9 times lower than the concentration in phosphogypsum from stack 2). For the sediment LD the total concentration of REE was 33.94 mg kg^{-1} (42 times smaller than the phosphogypsum stack 1 and 9 times smaller than the stack 2).

The ratio between the La/Yb in the RA soil was 153 and 113 in the PP soil; in the LD sediment the ratio was of 258, the highest observed La concentration in the soils and LD sediment. The predominance of La was expected because this element is more abundant in the soil than Yb (Tyler 2004).

In contrast, the soil RA showed most of heavy REE, indicating that the stacks have changed in some way the concentration of the elements on soil and sediment under its influence.

The REE La was most abundant in soil PP and sediment LD, while the Dy showed its highest abundance in the RA soil. This difference also suggests that the stacks may have influenced these results.

The Fig. 9 is a dendrogram to evaluate the concentration of REE within all samples of phosphogypsum. Two big similar groups were generated, being the first one formed by the samples of phosphogypsum on stack 2, from AR and PP soils and from the LD sediment evaluated. The second group was formed by stack 1 samples, these results indicate that there was significant difference between the samples from both stacks, the separation into two relatively homogeneous groups indicates this is probably associated to the different phosphate origin from each stack, corroborating, as well, to the literature, which determines that the REE concentration in igneous phosphate rocks is higher than in sedimentary ones, as was observed throughout this work for most of the REE.

Table 3 Concentration (mg kg^{-1}) of rare earths in soil samples

Element	Earth crust[a]	AR	PP	LD	Sandy soil[b]	Soil in Japan[c]
La	35	14.5 ± 0.3	27.58 ± 0.6	29.47 ± 0.8	3.0 ± 0.3	15
Ce	66	0.14 ± 0.01	0.19 ± 0.01	0.28 ± 0.01	21 ± 1	33
Sm	7	4.1 ± 0.2	2.68 ± 0.3	0.49 ± 0.1	0.39 ± 0.02	3.4
Eu	2.1	5.1 ± 0.3	1.45 ± 0.2	0.76 ± 0.2	<0.04	0.8
Dy	4.5	33.1 ± 0.7	1.47 ± 0.2	2.80 ± 0.2	<3	3
Yb	3.1	0.095 ± 0.02	0.243 ± 0.2	0.144 ± 0.1	1.5 ± 0.1	1.8

[a] Tyler 2004

[b] Oliveira 2012

[c] Uchida et al. 2007

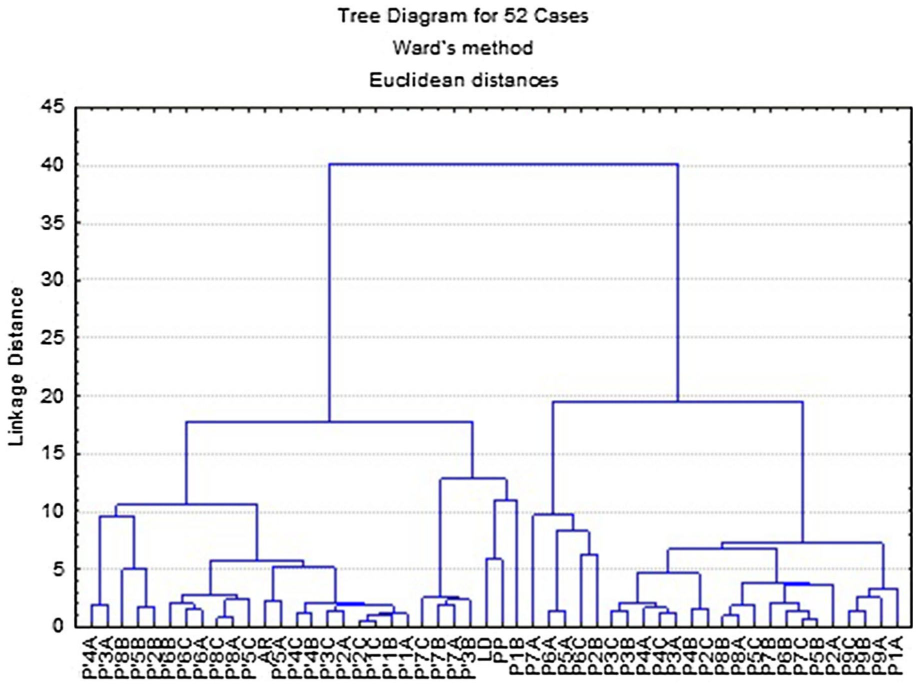

Fig. 9 Dendrogram considering the concentration of REE analyzed all sets of samples

Conclusions

The results found (ΣREE the order of 1432 mg kg^{-1} in stack 1 and 330.5 mg kg^{-1} in the stack 2) suggests that the phosphogypsum analyzed has a high content of REE when compared to background values of environmental samples.

The heterogeneity in the distribution of the REE in the depth suggests that the chemical composition of the phosphogypsum depends on the nature of the phosphate rock. The phosphogypsum evaluated in two stacks showed notable differences due to the type of the original rock: igneous or sedimentary. These elements may be used as tools in the study for differentiation of the original rock.

In stack 1, levels of Ce are also higher than in the stack 2, the elements stays within the range. The use of Phosphogypsum can cause environmental problems because of the concentration of this element by-product as soil conditioner in agriculture.

There was no leaching of the REE inside the profile of phosphogypsum stacks, and that the occurrence of REE in phosphogypsum is associated with the formation of sulphates, carbonates, fluorides and phosphates of these elements.

The concentration of REEs, as determined in the Reference Area in soil, was generally lower than the values determined by Tyler (2004) for the terrestrial crust, except for Eu and Dy.

When the concentrations of REE in the phosphogypsum are too high, this by-product can have a new use, as a REE source for high technology industry utilization, once there was a considerable raise in the demand of these elements worldwide.

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