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DETERMINATION OF REEs IN AGRICULTURAL SOILS OF PERNAMBUCO BY THE NEUTRON ACTIVATION TECHNIQUE

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ABSTRACT

The indiscriminate use of phosphate fertilizers causes adverse effects on biota, mainly due to the contaminants present in the rocks used in their manufacture. Among these contaminants, stand out the Rare Earth Elements (REEs) because of the significant increase in the use in several technological areas, such as in vehicle catalysts and also in fertilizer enrichment. In order to evaluate the levels of La, Sm, Nd, Yb and Lu by the Instrumental Neutron Activation Analysis (INAA), the present study aims to survey the ETRs in agricultural soils in Pernambuco/Brazil. For this study, 120 soil samples with a depth of 20 cm were collected in the main vegetable producing regions of the Metropolitan Region of Recife (RMR), evaluating organic and conventional crops with and without influenced by automotive vehicles. The results obtained when compared to the Netherlands reference values defined by the National Institute of Health and Environment (RIVM). The results were higher in all points for La (35 mg.kg-¹ at 85 mg.kg-¹) Yb, (4 mg.kg-¹ at 11 mg.kg-¹) and Lu (0.3 mg.kg-¹ at 0.7 mg.kg-¹ at 4 mg.kg-¹). For Nd (9 mg.kg-¹ at 137 mg.kg-¹) the concentrations were above the values reported by RIVM in 4 points. Comparing the types of crops evaluated with the literature, the results are found was above for all elements analyzed. It may be related to the increase in the use of phosphate fertilizers. However, in environments using smaller amounts of additives, the results were also significant and the more detailed studies are needed to evaluate other possible contamination pathways.

1. INTRODUCTION

The group of the Rare Earth Elements (REEs) consists of 17 elements, which integrate the series of the lanthanides, the scandium (Sc) and the yttrium (Y), according to IUPAC (International Union of Pure Applied Chemistry) (Martins; Isolani, 2005). Due to their atomic weights, ionic rays and, therefore, physical and chemical similarities in properties, are classified as light (La, Ce, Pr and Nd), intermediates (Sm, Eu, Gd, Ty, Dy and Ho) and heavy

(Er, Tm, Yb, Lu, Y e Sc), representing a geochemically coherent group (VERMEIRE et al., 2016; SAAZ et al., 2015).

These elements have become known to a large public in recent years due to the great of supply for the high-tech sector and are therefore used in current or emerging alternative energy and digital equipment (BRIOCHI et al., 2013). Moreover, due to the strong affinity for oxygen, these elements are commonly found in phosphates, nitrates, oxides and clayey sediments, and are therefore present in significant quantities in fertilizers as a subproduct in the process (Sadeghi et al., 2015).

Although they already contain ERRs in fertilizers, there are countries that develop these inputs by adding even more ERRs, this enrichment process has been done for more than 20 years to increase desorption of micronutrients to improve plant development, increased plant growth, improved drought resistance and acid stress (Pang et al., 2002). Some reports in the literature suggest this improvement in some horticultural species (DIATLOFF et al., 2008). However, its essentiality is still unknown and the critical appraisal of these claims has been difficult because of the ambiguities of the results. Thus arousing the interest of the scientific community in the evaluation of this efficiency.

In order to evaluate the development of plants under controlled concentrations of REE's, Diatloff et al. (2008) evaluated the absorption of La and Ce in mungbean and maize grown under controlled conditions and verified that the concentrations of these elements did not help the growth of the analyzed plants, but decreased growth, root function and consequently nutritional status of the mungbean from a give concentration (0.2 μM). However, in smaller concentrations had positive effects on the growth of the same vegetable. This corroborates with the results of soils evaluated by Wang and Liang (2014), since they verified that the low concentrations of REEs tend to increase the desorption of P facilitating in the process of assimilation of this micronutrient to the plant.

According to Saatz et al. (2015), the results described in the literature are inconsistent and come from differences in the form and concentration of the application, as well as in plant species or due to the behavior of the element itself.

It is important to emphasize that the indiscriminate use of RREs can cause adverse effects in the environment, due to their capacity to bioaccumulate, especially taking into account long-term applications. Thus, global use of these inputs, as well as the lack of cost-effective recycling, makes them potentially emerging pollutants (Saaz et al., 2015).

Thus, these sources of contamination of REEs are important entry routes for contamination in soils, mainly agricultural ones as they are the main source of nutrients for the plants, and can be accumulated for long periods bringing health risks to final consumers due to toxicity (Sadeghi et al., 2015).

Therefore, studies have been carried out for the background survey on the agricultural soils and determination of the REEs levels. Based on this, the objective of this work was to survey these elements in the agricultural soils of the main producing regions of the Metropolitan Region of Recife in Pernambuco - Brazil, in order to evaluate the levels of La, Sm, Nd, Yb and Lu in crops with and without vehicle influence and in organic cultures using the technique of Instrumentation Neutron Activation Analysis (INAA).

2. MATERIALS AND METHODS

2.1. Study area

This study was carried out in two different regions in the state of Pernambuco in Brazil, in the Metropolitan Region of Recife (RMR) and Zona da Mata, with soils of characteristic mixed and predominantly clayey, respectively (CUNHA FILHO, 2013; FREIRE, 2006).

Table 1 presents the points collected with their respective satellite locations, the type of cultivation carried out in each soil and the number of points sampled.

Region	Coordinates	Cultivated area	Type of crop	Number of points sampled	Identification of points
RMR	8°04'00,1"S e 34°56'40,7"W	7 ha	Conventional with vehicular traffic	2	BR – 1 BR – 2
Zona da Mata	8°08'26,6"S e 35°18'14,9"W	20 ha	Conventional with vehicular traffic	3	Figueira 0 – 50 m Figueira 50 – 100 m Figueira 100 – 150 m
Zona da Mata	8°08'23,5"S e 35°18'37,0"W	40 ha	Conventional	2	Natuba 1 Natuba 2
Zona da Mata	8°04'12,4"S e 35°17'41,8"W	50 ha	Conventional	1	Oiteiro
Zona da Mata	8°03'32,3"S e 35°17'55,3"W	7 ha	Organic	1	Palmeira
Zona da Mata	8°00'53,0"S e 35°16'24,6"W	1 ha	Organic	1	Serta

Table 1. Distribution of collection points with their respective locations.

In the points collected, it is common the use of cattle and poultry manure as organic matter. There is also in conventional crops the use of inorganic and organic fertilizers, in addition to the application of calcium carbonate. The application is made directly to the soil, when it comes to granular fertilizers, and directly to the leaf when it comes to liquid products. These applications in the areas of Figueira, Natuba and Oiteiro are performed daily, since the areas usually present cultures in different stages of development (CUNHA FILHO, 2013).

2.2. Sample collection and preparation

About 10 soil sample were collected at each point, totaling 100 sample, using a 7 cm-diameter, 50 cm-long pipe steel, at a depth of 0 to 20 cm, composing 10 composite samples, which were sent to the environmental analysis laboratory of the CRCN-NE / CNEN (Northeastern Brazilian Regional Center of Nuclear Science/Brazilian Nuclear Energy Commission) to be treated and sent to CRPQ/IPEN-CNEN (Research Reactor Center/Institute of Energy and Nuclear Research - Brazilian Nuclear Energy Commission) in São Paulo, Brazil. The samples were dried in an oven at 60ºC until constant weight, pulverized to a particle size of 80 μm to ensure a good homogenization and consequently obtain good geometry.

2.3 Analysis by INAA

In the present work, the comparative method of Instrumental Neutronic Activation Analysis (INAA) was used to determine the elements La, Nd, Sm, Yb and Lu. For this, approximately 100 mg subsamples were irradiated along with patterns of the chemical elements of interest, using as reference standard material Granite GS-N of the Association Nationale de la Recherche Technique (ANRT).

The samples were irradiated for a period of 8 hours under thermal neutron flux of about 1012 ncm^{-2} s^{-1} in the IPEN - CNEN on the IEA-R1 reactor. After a seven day decay period the gamma activities induced from the radionuclides of interest were measured for 1.5 h on a Canberra GC2018 HPGe hyperpure germanium detector coupled to a Canberra DSA - 1000 multi - channel analyzer.

Gamma-ray spectra were collected and processed using the Genie 2000 program, version 3.1 (Canberra). The data were then treated and the concentrations of the elements of interest were determined.

3. RESULTS AND DISCUSSION

In figure 1 it is possible to observe the behavior of the lanthanides analyzed at the collection points sampled. It is observed that the highest concentrations are in the Natuba 1 point, an area diagnosed as the largest user of fertilizers and agrochemicals due to the demand in its production. However, by comparing the Natuba 1 and 2 points, the highest concentrations are found in point 1, possibly due to the leaching process of the elements, because it is a lower point compared to point 2.

In relation to the concentration found in the Oiteiro region, when compared to Natuba 1, the values were lower for all elements analyzed. In this region the use of fertilizers may have contributed to the difference of these results, once Oiteiro uses a smaller quantity of these inputs, besides the use of the area for agricultural purposes is more recent. However, this difference was not significant according to the analysis of variance with 0.05% significance and with a p-value of 0.16, taking into account points Oiteiro, Natuba 1 and 2.

Applying the same test with a p-value of 0.18 to evaluate the vehicular influence with the analyzed elements taking into account the distances of the highway in Figueira point and making a comparison of the areas BR 1, BR 2 and Figueira, it is verified that there is no relation between vehicular influence and the elements analyzed.

At points BR 1 and 2, because they were located in the RMR and were more influenced by vehicular traffic, higher concentrations were expected in relation to the Figueira region, which had a lower impact. However, this region has a greater use in the use of chemical fertilizers, which may have contributed to the expressive values of Nd and Sm obtained.

It is worth noting that the influence of vehicle traffic on the studied elements is related to the use of catalysts, but as it is a relatively new technique, there is still no significant influence on the concentrations of these elements in road soils (CGEE, 2013). However, it is important to obtain data on this information to compose a database and in future to make comparisons and evaluate the influence of these elements over the years.

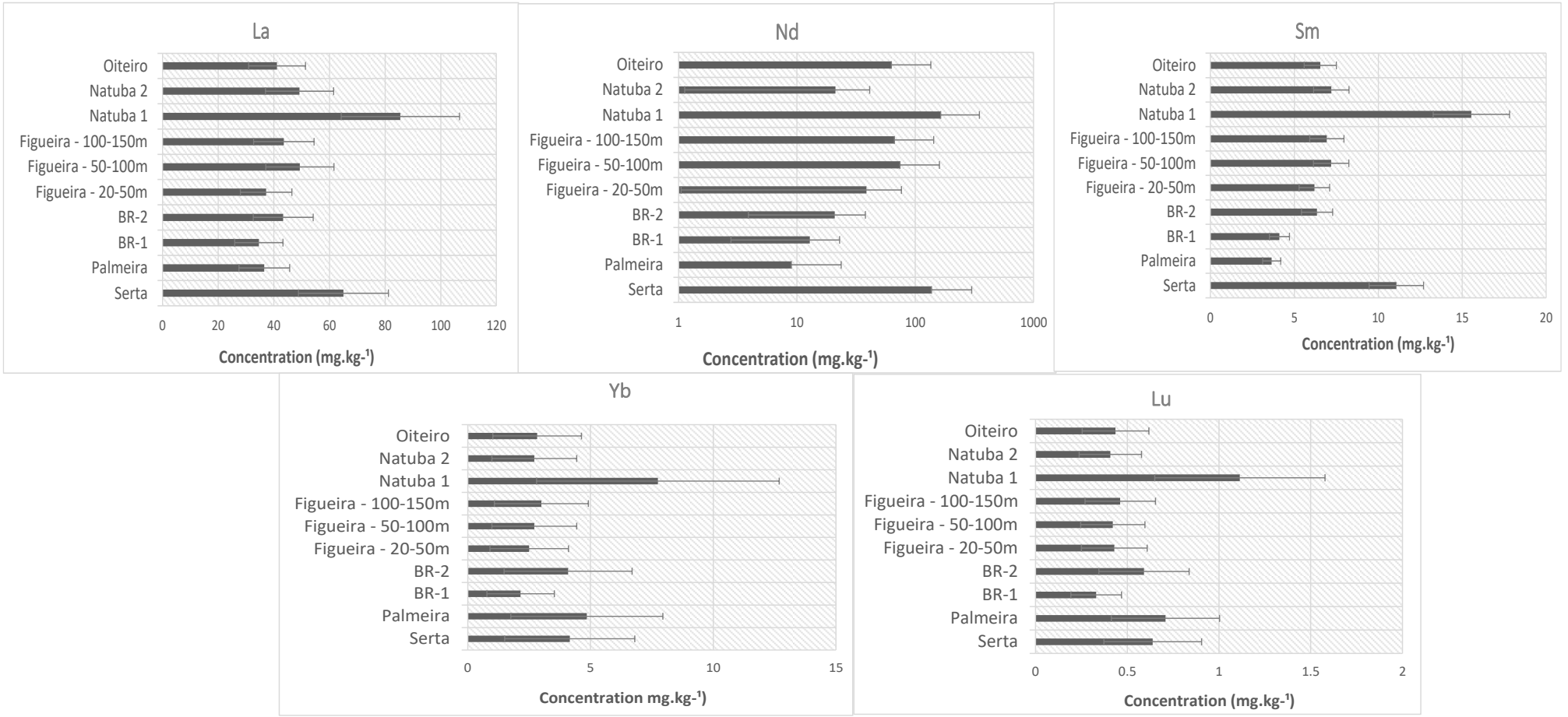

Figure 1. Concentration of the elements La, Nd, Sm, Yd and Lu in the different soils analyzed.

Taking into account the different types of cultivation in the study region, average results were obtained for each possible route of contamination of these elements, which were compared with the literature (figure 2). Based on the information on land crust and Brazilian soils described by Paye et al. (2015), in addition to the reference values of the Netherlands for soils of the National Institute of Health and Environment (RIVM), it was possible to obtain parameters for comparison in the present work.

The results show an anthropic action indicative, obtaining values above the standards established for comparison in all elements analyzed.

In Figure 2, it is also observed that conventional cultivation without the influence of vehicular traffic presented the highest concentrations in relation to organic and conventional cultivation with the influence of vehicular traffic, giving an indication that there is not yet a significant preponderance of these elements in soils from the emissions of the motor vehicles. It is worth noting that, applying the variance test with 0.05% significance and p-value of 0.13, comparing the different cultures, this difference was not statistically significant.

Therefore, this does not characterize a contamination, since from the analyzes of variance the results did not present significant differences, taking into account the possible sources of pollution. There is only a slight indication of the indiscriminate use of fertilizers.

It is also important to highlight that the soil characteristic in the Zona da Mata region is predominantly clayey (CUNHA FILHO, 2013), which may have provided more expressive concentrations of REEs in relation to the values found in points Br 1 and 2 (RMR), besides the quantitative use of the fertilizers in the conventional crops of Zona da Mata.

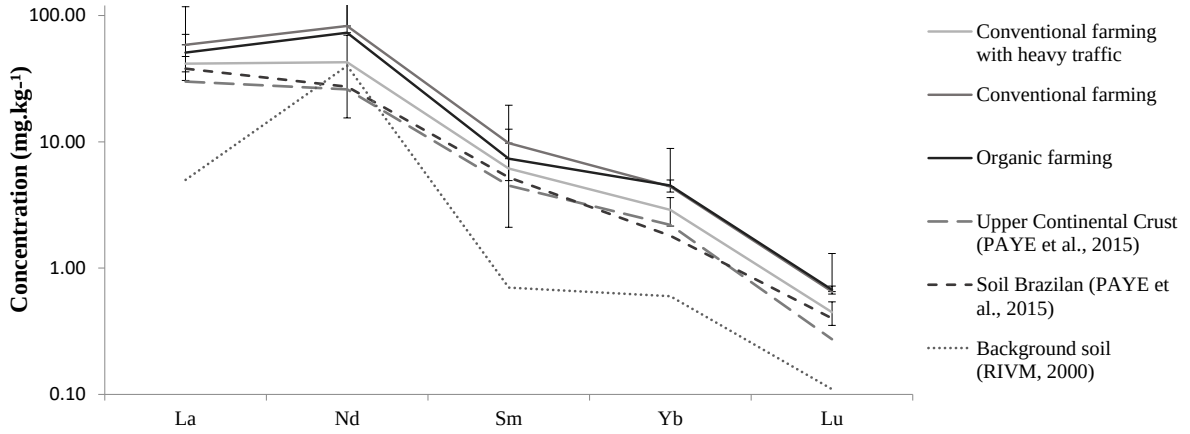

Figure 2. Distribution of the mean values of REEs in the different types of culture analyzed.

In order to evaluate the behavior of the elements in relation to the standards a Pearson correlation was made (table 1), and the results reveal a positive correction between the behavior obtained in the present study to that found in Brazilian soils, in the upper terrestrial crust and the values of the Netherlands.

Table 1. Pearson's correlation coefficient on the analyzed points together that the values used as reference.

	La	Nd	Sm	Yb	Lu
La	1				
Nd	0.76	1			
Sm	0.97	0.86	1		
Yb	0.84	0.62	0.85	1	
Lu	0.86	0.64	0.82	0.97	1

4. CONCLUSION

• There is a tendency for increased concentration of REEs to have been influenced by the indiscriminate use of fertilizers.
• There was no relation between the analyzed elements and the influence of vehicular traffic.
• There was no significant difference between organic cultivation and conventional cultivation with or without vehicular influence.
• The analyzed soils are above the values found in Brazilian soils.
• The behavior of the elements analyzed was consistent with that found in the literature.
• The average results found were higher than the standard values used in the present study, being an indication of anthropic action.

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REFERENCES

1. CGEE - Centro de Gestão e Estudos Estratégico. Usos e aplicações de Terras Raras no Brasil: 2012-2030. Brasília – DF, 254p. (2013)
2. Cunha Filho, F. Metais pesados em solo, água e hortaliças em áreas produtoras de olerícolas na zona da mata de Pernambuco. *UFPE*. 78p (2013).
3. E. Diatloff, F. W. Smith, C. J. Asher. “Effects of Lanthanum and Cerium on the Growth and Mineral Nutrition of Corn and Mungbean”. *Annals of Botany*. v. 101, pp. 971-982 (2008).
4. Freire, E. M. M. (2006). Lead concentration evaluation in soil, water and lettuce 330 (Lactuca sativa L.) cultivation near the highway BR-101 and BR-232 in the 331 neighborhood of Curado, Recife-PE. MSc Dissertation. Institute of Technology of Pernambuco (in Portuguese), Brazil. Dissertation. Instituto de Tecnologia de 333 Pernambuco. 60.
5. H. S. Paye, J. W. V. Mello, G. R. L. M. Mascarenhas, M. Gasparon. Distribution and fractionation of the rare earth elements in Brazilian soils. *Journal of Exploration*. v. 161, pp. 27-41 (2016).

6. J. Saatz, D. Vetterlein, J. Mattusch, M. Otto, B. Daus. The influence of gadolinium and yttrium on biomass production and nutrient balance of maize plants. Environmetal pollution. v. 204, pp. 32-38 (2015).
7. L. Wang, T. Liang, "Effects of exogenous rare earth elements on phosphorus adsorption and desorption in different types of soils". *Chemosphere* v. 103, pp. 148-155 (2014).
8. M. Sadeghi, S. Albanese, G. Morris, A. Landenberger, M. Andersson, C. Cannatelli, A. Lima, B. Vivo. "REE concentrations in agricultural soil in Sweden and Italy: Comparison of weak MMI extraction with near total extraction data". Applied Geochemistry. v. 63, pp. 22-36 (2015).
9. L. Brioschi, M. Steinmann, E. Lucot, M. C. Pierret, P. Stille, J. Prunier, P. M. Badot. "Transfer of rare earth elements (REE) from natural soil to plant systems: implications for the environmental availability of anthropogenic REE". *Plant Soil*. v. 366, pp. 143-163 (2013).
10. M. L. Vermeire, S. Cornu, Z. Fekiacova, M. Detienne, B. Delvaux, J. T. Cornélis. "Rare earth elements dynamics along pedogenesis in a chronosequence of podzolic soils". *Chemical Geology*. v. 446, pp. 163-174 (2016).
11. RVIH - Rijksinstituut voor Volksgezondheid en Milieu (2011). A. Dusseldorp, D.J.M. Houthuijs, A.J.P. van Overveld, I. van Kamp, M. Marra. 'Handreiking geluidhinder wegverkeer Berekenen en meten" Rapport 609300020/2011.
12. T. S. Martins, P. C. Isolani. "Terras raras: aplicações industriais e biológicas". *Quim. Nova*. v. 28, pp. 111-117 (2005).
13. X. Pang, D. Li, A. Peng. "Application of Rare-earth Elements in the Agriculture of China and its Environmental Behavior in Soil". *Environ Sci & Potlut*. v. 2, pp-143 - 148 (2002).