Journal of Environmental Chemistry and Ecotoxicology Vol. 3(4), pp. 86-92, April 2011
Available online http://www.academicjournals.org/jece
ISSN-2141-226X ©2011 Academic Journals

Full Length Research Paper

Evaluation on rare earth elements of Brazilian agricultural supplies

C. Turra*, E. A. N. Fernandes and M. A. Bacchi

Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Piracicaba, SP, Brazil.

Accepted 1 March, 2011

This work focuses on the determination of rare earth elements (REE) in Brazilian agricultural supplies by instrumental neutron activation analysis (INAA). The results obtained have shown that La, Ce, Nd, Sm, Eu, Tb, Yb, Lu and Sc are present within a large range of mass fractions in the agricultural supplies analysed. The thermophosphate and single superphosphate showed the highest mass fractions of REE. Considering the recommended dose and long-term use, NPK fertilizers, single superphosphate and thermophosphate can significantly increase the content of REE in soil and may cause harmful effects to environment and humans.

Key words: Agricultural supplies, rare earth elements, lanthanoids, phosphate fertilizer, INAA.

INTRODUCTION

The rare earth elements (REE) are in Group IIIB of the periodic table, including Sc, Y and the lanthanoids (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) (IUPAC, 2005). REE have similar physico-chemical properties (Evans, 1990) and, despite the denomination, they cannot all be considered rare in nature (Hu et al., 2004), since the abundance of Ce in soil is similar to Cu and Zn (Tyler, 2004). Despite being present in plants, REE are not considered essential. Most of the uptake occurs by roots (Wyttenbach et al., 1998), but it can also occur through the surface of leaves after spraying or atmospheric deposition (Chua, 1998). Anyhow, REE have been used in agriculture applied to leaves, seeds and roots (Diatloff et al., 1996).

The application of fertilizers containing REE has being claimed to increase growth and productivity of plants (Challaraj et al., 2010), however this effect is not yet clear (Tyler, 2004; Shi et al., 2006). On the other hand, the accumulation of REE in the soil may have a toxic effect on macro fauna (Li et al., 2010) and micro fauna (Xu and Wang, 2001; Chu et al., 2001). Moreover, excessive application in agriculture may cause harmful effects to humans by bioaccumulation along the food chain.

Studies conducted in areas rich in REE reported that, constant exposure can cause damages in the circulatory, immunologic (Zhang et al., 2000), digestive (Zu-Yi and Xu-Dong, 2009; Li et al., 2010), respiratory (Censi et al., 2011), and nervous systems (Zhu et al., 2005), as well as can decrease intelligence quotient in children (Fan et al., 2004), and can start development of arteriosclerosis and pneumoconiosis (Sabbioni et al., 1992).

Mixture of REE in fertilizers has been used in Chinese agriculture to improve the nutrition of plants for more than 25 years. In 1986, the first commercial fertilizer with REE was registered in China under the name “Changle”, having in its composition La_2O_3 (25 to 28%), CeO_2 (49 to 51%) and Nd_2O_3 (15 to 17%) (Hu et al., 2004). Studies have reported both positive (Hu et al., 2004; Wang et al., 2001) and negative effects (Diatloff et al., 1995; Barry and Meehan, 2000; Babula et al., 2008) in plants after application of REE fertilizers. Two rice areas receiving REE fertilizers presented mass fractions of La in soil (42.1 and 83.3 mg kg^{-1}) at critical levels in terms of environmental safety (Zeng et al., 2006). In Brazil, as in many other countries, there is no recommendation to add REE to fertilizers.

Nevertheless, besides providing nutrients for plants, fertilizers can also have impurities as metals and other elements. There is little information regarding the presence of REE in agricultural supplies available worldwide.

*Corresponding author. E-mail: christian.turra@gmail.com.

Table 1. Agricultural supplies collected for this study, main chemical composition and recommended use.

Supplies	Chemical composition	Recommended use
Agro-silicon	36% CaO, 9% MgO, 23% SiO_2	Corrective
Calcium	22 % Ca	Fertilizer
Calcium nitrate	24% Ca, 17% N, 59% O	Fertilizer
Chicken manure	2-3.5 % N, 2-4% P_2O_5, 1- 2% K_2O	Fertilizer
Copper oxychloride	48 – 52 % Cu	Fertilizer and fungicide
Cow manure	1-2% N, 0.8-1.4% P_2O_5, 1-1.8% K_2O	Fertilizer
Cromcitrus	2 – 4% Mn, 3 – 5% Zn	Fertilizer
Dolomite lime 1	25 – 35% CaO, 12 – 15% MgO	Corrective
Dolomite lime 2	25 – 35% CaO, 12 – 15% MgO	Corrective
Hydrated lime	40 % Ca, 17% Mg	Fertilizer and fungicide
Iron	6 % Fe	Fertilizer
Lime sulphur powder	3.5% Ca (total) and S	Fertilizer and insecticide
Magnesium nitrate	10.7% N, 15.5% Mg	Fertilizer
Magnesium sulphate	9.4% Mg, 12% S	Fertilizer
Monoammonium phosphate (MAP)	48% P_2O_5, 9% N	Fertilizer
NPK	%N, %P_2O_5, %K_2O variable	Fertilizer
Reactive phosphate	24 – 27% total P_2O_5	Fertilizer
Single superphosphate	18% P_2O_5, 18-20% Ca, 12-20% S	Fertilizer
Sulphur	30 – 40 % S	Fertilizer
Thermophosphate	16-18% P, 16-18% Ca, 6-7%Mg	Fertilizer

Therefore, it is important to assess the contents of REE in these supplies in order to regulate their correct use in agriculture. This work focuses on the determination of REE by instrumental neutron activation analysis (INAA) in some agricultural supplies used in Brazil. The determination will allow better use of agricultural supplies and the identification of possible sources of REE contamination.

MATERIALS AND METHODS

Agricultural supplies were sampled in different farms located in the state of São Paulo, Brazil. Samples are listed in Table 1, together with the main chemical composition and the recommended use of each product. At Centro de Energia Nuclear na Agricultura (CENA), in Piracicaba, materials were oven-dried and the particle size was reduced to less than 0.5 mm. Test portions of 300 mg were directly weighed into high purity polyethylene vials. For quality control purposes, certified reference materials of geological matrices (IAEA-Soil 7 and SRM-2710 Montana Soil) were added to the analytical series.

Empty vials were also included for blank correction.Irradiation was carried out for 8 h at a thermal neutron flux of 8.5×10^{12} cm^{-2} s^{-1} in the nuclear research reactor IEA-R1 of the Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear (IPEN/CNEN), São Paulo. The material was transported back to CENA, where the induced radioactivity was measured at four decay periods, that is 4, 7, 15 and 40 days after irradiation. Germanium detectors with 50 and 55% relative efficiencies in the 1332 keV photopeak from ^{60}Co were used for measurements. Mass fractions were calculated by the k_0-method using the in-house software package Quantu (Bacchi and Fernandes, 2003).

RESULTS AND DISSCUSSION

Data obtained for the certified reference materials (Table 2) demonstrated that the analytical procedure was adequate for the determination of nine REE, that is, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu and Sc, since there is a good agreement with the values provided in the certificates. For some samples, it was necessary to correct the results of La, Ce, Nd and Sm due to uranium interference, which has to be considered when the concentration of U exceeds 5 mg kg^{-1} (Kuleff and Djingova, 1990). The highest values of U were found in thermophosphate 2 (49.3±1.7 mg kg^{-1}), thermophosphate 146.2±1.4 mg kg^{-1}), NPK 4-20-20 (39.4±1.1 mg kg^{-1}), reactive phosphate (39.3±1.4 mg kg^{-1}) and single superphosphate (38.2±1.7 mg kg^{-1}).

The largest relative interference was observed for Sm (16%) in hydrated lime. For Nd, the largest interference was 8% (in hydrated lime), the same maximum value found for Ce (in lime and limestone 2). For La, the relative interference was lower than 2% in all samples. Considering these results, it can be assumed that, after suitable correction, the uranium interference did not impair the quality of results.

Results showed that La, Ce, Nd, Sm, Eu, Tb, Yb, Lu and Sc are present at variable levels in the agricultural supplies (Table 3), being higher mass fractions found in phosphates and NPK fertilizers. The two limes analyzed showed higher mass fractions of La, Ce and Nd and lower of Eu compared to the values obtained in Florida,

Table 2. Mass fractions and standard deviations (mg kg-1) of REE obtained for the reference materials IAEA Soil 7 and SRM 2711 Montana Soil compared to data provided in the respective certificates

Element	IAEA Soil 7		SRM 2711 Montana Soil	
	Obtained value	Confidence internal	Obtained value	Information value
La	27.7 ± 0.6	27 – 29	40.7 ± 0.8	40
Ce	60.5 ± 1.1	50 – 63	71.5 ± 1.2	69
Nd	31.1 ± 0.6	22 - 34	32.0 ± 0.7	31
Sm	5.0 ± 0.2	4.8 – 5.5	6.1 ± 0.2	5.9
Eu	1.02 ± 0.03	0.9 – 1.3	1.08 ± 0.04	1.1
Tb	0.63 ± 0.04	0.5 – 0.9		-
Yb	2.37 ± 0.06	1.9 – 2.6		-
Lu	0.32 ± 0.02	0.1 – 0.4		-
Sc	8.33 ± 0.04	6.9 – 9.0	9.07 ± 0.05	9.0

Table 3. Mass fractions and standard deviations (mg kg-1) of REE determined in agricultural supplies, also including values from literature for NPK fertilizers or lime

	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Sc
Agrosilicon	9.3 0.2	77.8 1.6	<11	1.74 0.04	0.34 0.01	0.06 0.005	1.13 0.007	0.17 0.044	3.55 0.001
Calcium nitrate	2.17 0.001	3.10 0.02	<1.95	0.18 0.0025	0.033 0.001	<0.031	<0.077	<0.005	<0.004
Calcium	2.09 0.02	2.69 0.10	<1.68	0.13 0.0017	0.031 0.0001	<0.029	<0.06	<0.012	<0.008
Chicken manure	1.59 0.07	4.5 0.02	2.8 0.26	0.31 0.004	0.094 0.0007	0.065 0.004	0.18 0.015	0.085 0.067	0.48 0.002
Copper oxychloride	0.50 0.02	0.61 0.011	<2.26	0.08 0.0008	0.02 0.002	<0.04	<0.2	<0.018	0.069 0.0004
Cow manure	6.76 0.38	23.8 0.59	6.57 1.16	0.92 0.09	0.28 0.013	0.25 0.017	0.66 0.001	0.16 0.009	3.02 0.037
Cromcitrus	<0.25	<7.0	<30	<0.26	<0.42	<0.74	<0.56	<0.23	<0.05
Dolomite lime 1	7.77 0.078	17.1 0.28	8.0 0.25	1.35 0.007	0.22 0.007	0.25 0.046	0.67 0.007	0.14 0.006	2.01 0.057
Dolomite lime 2	6.78 0.071	13.1 0.28	7.14 0.028	1.35 0.064	0.24 0.001	0.15 0.005	0.55 0.003	0.12 0.002	0.72 0.004
Hydrated lime	2.5 0.04	3.4 0.25	2.36 0.37	0.35 0.01	0.07 0.001	<0.028	0.146 0.001	<0.017	0.47 0.005
Iron	<0.48	<0.68	<1.2	<0.022	<0.007	<0.036	<0.135	<0.023	0.042 0.0008
Magnesium sulphate	<0.61	<0.55	<1.57	<0.19	<0.007	<0.026	<0.020	<0.011	<0.01
Magnesium nitrate	<0.31	<0.22	<1.8	<0.02	<0.008	<0.02	<0.023	<0.04	<0.04

Table 3. Contd.

Monoammonium phosphate (MAP)	0.97 0.10	7.3 0.43	<2.4	<0.21	<0.008	<0.03	<0.025	<0.028	0.69 0.01
NPK 10 10 10	372 3	770 9	360 2.14	47 0.86	10.6 0.14	3.04 0.064	1.78 0.071	0.53 0.024	8.18 0.071
NPK 20 0 10	0.31 0.02	0.45 0.06	<5.8	0.05 0.0009	0.008 0.0003	<0.04	<0.06	<0.03	0.04 0.001
NPK 12 6 12	237 4	538 13	250 3	32 2	7.00 0.12	1.82 0.04	1.08 0.01	0.26 0.002	5.41 0.004
NPK 4 20 20	421 0.02	875 2	443 7	70 1	18.3 0.43	6.32 0.03	5.21 0.06	1.54 0.04	23.1 0.002
NPK 4 14 8	534 1	1181 7	571 0.01	77 1.5	17.1 0.01	4.57 0.03	2.03 0.13	0.55 0.04	15.2 0.37
NPK 25 5 20	91 0.78	211 1.4	101 12.3	13 1.1	2.73 0.2	0.72 0.017	<0.09	0.12 0.046	3.54 0.28
NPK 20 5 15	368 8.6	839 1.4	379 11.5	45 0.9	10.8 0.072	2.45 0.05	1.71 0.11	0.12 0.02	6.8 0.043
Single superphosphate	673 7	1499 29	770 16	122 2	32.5 0.15	6.53 0.19	8.8 0.08	1.84 0.07	24.6 0.005
Sulphur	<0.50	<0.27	<2.8	<0.06	<0.029	<0.027	<0.06	<0.052	<0.010
Reactive phosphate	99 0.1	164 0.7	110 0.7	17 1.7	3.59 0.04	2.38 0.01	6.1 0.6	1.4 0.07	3.7 0.02
Thermophosphate 1	755 4.3	1575 7	748 31	105 3	24.5 0.07	8.03 0.04	10.4 0.07	1.8 0.09	23.9 0.14
Thermophosphate 2	673 8	1430 14	687 11	102 3	24.5 0.28	8.54 0.02	10.8 0.07	2.2 0.17	26.5 0.07
NPK[25]	<0.5-619	<3 -744	<5 - 214	<0.1-42	0.2 - 12	0.5-3.2	0.2-5.5	0.16-0.85	-

United Sates (Wutscher and Perkins, 1993). Sc is known as tracer of geological material (Fernandes, 1992). Typical values for Sc in soils lie between 0.5 and 45 mg kg^{-1} (Markert, 1998). The agricultural supplies with geological origin presented values within this range. The mass fractions of REE in NPK fertilizers analyzed in Spain showed values varying in a similar range compared to the NPK fertilizers evaluated here (Table 3). NPK is considered a compound fertilizer because it contains two or more primary nutrients (Otero et al., 2005), and the content of REE is somehow related to the amount of P in the fertilizer. Total REE in NPK and phosphate fertilizers are shown in Table 4. The results evidenced that the highest amounts of REE are normally found in fertilizers containing phosphorous in the composition. For the NPK fertilizers without phosphorous ("zero" of P in NPK formulation), the mass fractions of REE were significantly lower than for NPK fertilizers with

Table 4. Total REE found in fertilizers ordered according to the content of P_2O_5.

Fertilizer	% P_2O_5	Σ REE (mg kg^{-1})
NPK 20 0 10	0	3
NPK 25 5 20	5	420
NPK 20 5 15	5	1640
NPK 12 6 12	6	1060
NPK 10 10 10	10	1550
NPK 4 14 8	14	2370
Single superphosphate	18	3070
Thermophosphate 1	18	3190
Thermophosphate 2	18	2895
NPK 4 20 20	20	1810
Reactive phosphate	27	390
Monoammonium phosphate (MAP)	60	12

phosphorus**.** The results suggest that, the amount of REE in NPK fertilizers depends on P contents, but is most probably also related to industrial process and P source used in the formulation. For instance, monoammonium phosphate presented a low level of REE because its industrial process involves purification steps.

Brazil is the fourth world consumer of fertilizers, after China, India and the United States (ANDA, 2006). The country imports part of the phosphate applied in agriculture, mostly coming from Morocco (51%), Algeria (18%), Israel (17%) and also from Togo and Tunisia (13% together). The crops that most use fertilizers with P_2O_5 in the country are soybean, corn and sugar cane. The distribution pattern of REE in phosphates and NPK fertilizers is shown in Figure 1. The mass fraction of Ce was higher than La for all samples analyzed. In general, the samples showed the same REE distribution pattern of chondrite. However, Tb and Yb presented a different behavior in NPK fertilizers. The value of Yb (0.248 mg kg^{-1}) in chondrite is higher than Tb (0.058 mg kg^{-1}) and in the NPK fertilizers the values of Tb were higher than Yb (Table 4).

A study of phosphorite deposits in Pakistan showed enrichment of light REE (Javied et al., 2010). Some samples of NPK fertilizers analyzed in Spain also showed different distribution patterns for Tb and Yb, while others have La higher than Ce (Otero et al., 2005). The mass fractions of REE determined by INAA in Egyptian phosphate fertilizer ingredients were in descending order La>Ce>Sc>Eu (Abdel-Haleem et al., 2001), a different distribution pattern compared to that found in this study.

According to Asher et al. (1990), the recommended dose for REE fertilizer (e.g. Changle) is 600 to 675 g/ha, which represents an application of about 150 to 170 g of REE per hectare. The recommended application of REE is dependent on their bioavailability in soils, which in turn is mainly dependent on the exchangeable fraction of REE, strongly affected by the physico-chemical properties of soils (Liang et al., 2005). Considering that the recommended dose of thermophosphate ranges from 300 to 1500 kg/ha (Mitsui fertilizers, 2006), the amount of Ce applied would vary from 0.47 to 2.4 kg/ha and the total amount of REE coming from fertilizer would vary between 1 and 5 kg/ha. The average REE content in NPK fertilizers with phosphorous in the formulation was 1450 mg kg^{-1}. For a recommended dose between 100 and 400 kg/ha, the input of all REE is between 0.15 and 0.58 kg/ha for each application. Considering the large consumption of NPK fertilizers, that is 8.9 million tons per year in Brazil (ANDA, 2009), significant amounts of REE have been applied via this fertilizer.

Due to a low risk of REE leaching in groundwater (Hu et al., 2006) and the low REE mobility in soil (Kabata-Pendias and Mukherjee, 2007), the continuous application may lead to accumulation of REE in agricultural soils. In general, phosphate fertilizers are rich in REE (Tyler, 2004), however such elements are usually not considered as nutrients. Therefore, the possible effects of REE in plants and environment are not taken into account.

Conclusions

The amount of REE in the agricultural supplies was largely variable. The highest mass fractions of REE were found in fertilizers containing phosphate. In general, the REE distribution pattern in the supplies was similar to that of chondrite, except for Tb and Yb in NPK fertilizers. Considering the recommended dose and long-term use, NPK fertilizers, single superphosphate and thermophosphate can provide more REE than the recommended doses found in literature. Such high inputs can significantly increase the content of REE in soil, which may cause harmful effects to environment and humans.

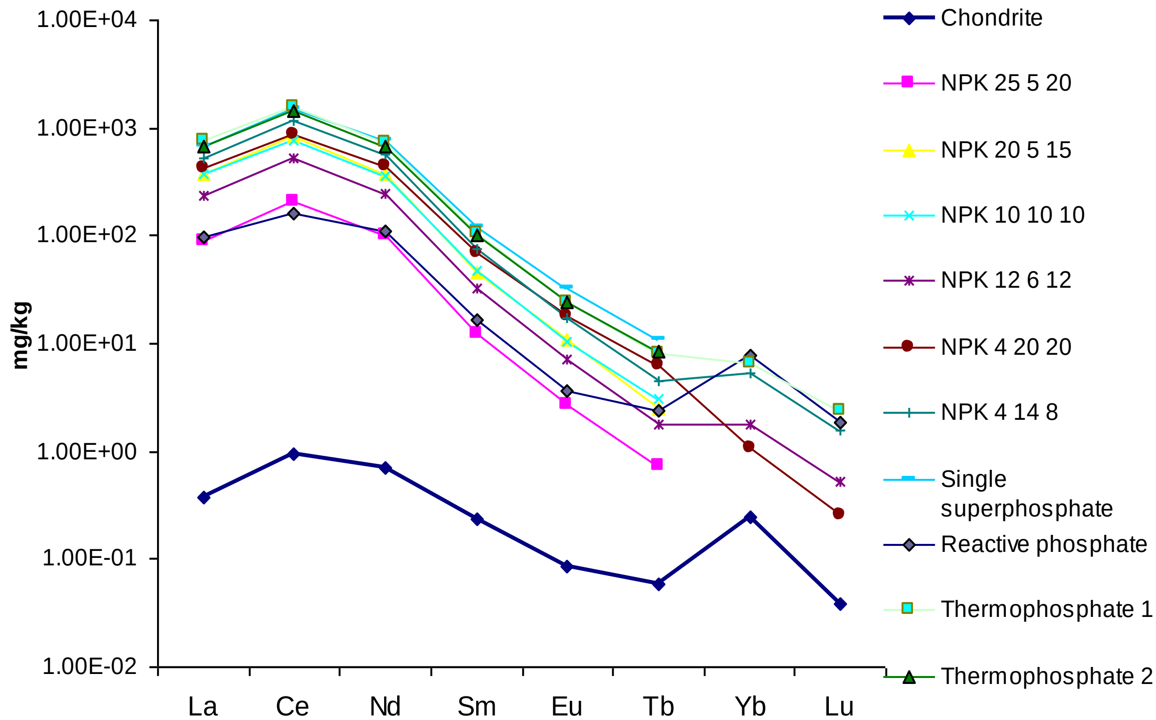

Figure 1. Distribution pattern of REE in NPK and phosphate fertilizers.

REFERENCES

Abdel-Haleem AS, Sroor A, El-Bahi SM, Zohny E (2001). Heavy metals and rare earth elements in phosphate fertilizers components using instrumental neutron activation analysis. Appl. Radiat. Isotopes, 55: 569–573.

ANDA (Agência Nacional de Difusão dos Adubos) (2006) Available at http://www.anda.org.br/estatisticas.aspx Accessed 12 April 2010

Asher CJ, Reghenzani JR, Robards KH, Tribe DE (1990). Rare earths in Chinese agriculture. *In* 'Report of an Australian Mission which visited China from 31 March–15 April 1990'. Aust. Acad. Technol. Sci. Eng., p. 54.

Babula P, Adam V, Opatrilova R, Zehnalek J, Havel L, Kizek R (2008) Uncommon heavy metals, metalloids and their plant toxicity: a review. Environ. Chem Lett., 6: 189-213.

Bacchi MA, Fernandes EAN (2003). Quantu – design and development of a software package dedicated to k_0-standardized NAA. J. Radioanal. Nucl. Chem., pp.257-577.

Barry MJ, Meehan BJ (2000). The acute and chronic toxicity of lanthanum to *Daphnia carinata*. .IUPAC. Recommendations 2005. Cambridge CB4 0WF, UK Chemosphere, 41: 1669-1674.

Censi P, Tamburo E, Speziale S, Zuddas P**,** Randazzo LA, Punturo R, Cuttitta A, Aricò P (2011). Yttrium and lanthanides in human lung fluids, probing the exposure to atmospheric fallout. J. Hazard. Mater., 186(2-3): 1103-1110

Challaraj EES, Vignesh V, Anandkumar B, Maruthamuthu S (2010). Bioaccumulation and physiological impact of rare earth elements on wheat (*triticum aestivum*) Indian J. Plant. Physiol*.,* 15(2): 177-180

Chu HY, Zhu JG, Xie ZB, Cao ZH, Li ZG, Zeng Q (2001). Effects of lanthanum on soil microbial biomass carbon and nitrogen in red soil. J. Rare Earths, 19: 63 – 66

Chua H (1998). Bio-accumulation of environmental residues of rare earth elements in aquatic flora *Eichhornia crassipes* (Mart) Solms in Guangdong Province of China. Sci. Total Environ., 214:79-85.

Diatloff E, Smith FM, Asher CJ (1995). Rare earth elements and plant growth. Effects of lanthanum and cerium on root elongation of corn and mungbean. J. Plant Nutr., 18: 1963–1976.

Diatloff E, Asher CJ, Smith FW (1996). Concentrations of rare earth elements in some Australian soils. Aust. J. Soil Res., 34:735-747.

Evans CH (1990). Biogeochemistry of the lanthanides. Plenum Press. New York. 8: 444

Fan GQ, Yuan ZK, Zheng HL, Liu ZJ (2004). Study on the effects of exposure to rare earth elements and health-responses in children aged 7– 10 years, J. Hyg. Res., 33:23– 28.

Fernandes EAN (1992). Scandium as tracer in the sugar and alcohol agroindustry. J. Radioanal. Nucl. Chem., pp.168-41.

Hu Z, Richter H, Sparovek G, Schnug E (2004). Physiological and biochemical effects of rare earth elements on plants and their agricultural significance: a review. J. Plant Nutr., 27: 183–220.

Hu Z, Haneklaus S, Sparovek G, Schnug E (2006). Rare earth elements in soils. Commun. Soil Sci. Plant Anal., 37(9): 1381-1420.

Javied S, Waheed S, Siddique N, Shakoor R, Tufail M (2010). Measurement of rare earths elements in Kakul phosphorite deposits of Pakistan using instrumental neutron activation analysis J Radioanal. Nucl. Chem., 284: 397–403

Kabata-Pendias A, Mukherjee AB (2007). Trace elements from soil to human. New York: Springer, 450 p.

Li J, Hong M, Yin X, Liu J (2010). Effects of the accumulation of the rare earth elements on soil macrofauna community. J. Rare Earths 28:957-964

Li XB, Yu XL, Wang TG, Su SY, Zhao K, Zhang XJ (2010). Effect of rare earth La_2O_3 on digestive system of the red-eared slider. Adv. Mater. Res., 108-111: 866

Liang T, Zhang S, Wang L, Kung H, Wang Y, Hu A, Ding S (2005). Environmental biogeochemical behaviors of rare earth elements in soil plant systems. Environ.Geochem. Health, 27: 301- 311

Markert B (1998). Distribution and biogeochemistry of inorganic chemical in the environment. In: G. Schüürmann and B. Markert (eds.), Ecotoxicology, John Wiley & Sons, Inc. and Spektrum Akademischer Verlag, Weinheim. pp. 165–222.

Mitsui Fertilizer Company (2006). Available at http://www.fertilizantesmitsui.com.br/template.php?page=produtos/produtos_yoorin Accessed 22 November 2009

Otero N, Vitòria L, Soler A, Canals A (2005). Fertiliser characterisation:

major, trace and rare earth elements. Appl. Geochem., 20: 1473–1488.

Sabbioni E, Pietra R, Gaglione P, Vocaturo G, Colombo F, Zanoni M, Rodi F (1992). Long-term occupational risk of rare-earth pneumoconiosis. A case report as investigated by neutron activation analysis. Sci. Total Environ., 26: 19-32.

Shi P, Huang ZW, Chen GC (2006). Influence of lanthanum on the accumulation of trace elements in chloroplasts of cucumber seedling leaves. Biol Trace Elem. Res., 109: 181–188

Tyler G (2004). Rare earth elements in soil and plant systems – a review. Plant Soil 267: 191–206.

Wang Z, Liu D, Lu P, Wang C (2001). Accumulation of rare earth elements in corn after agricultural application. J. Environ. Qual., 30: 37-45.

Wyttenbach A, Furrer V, Schleppi P, Tobler L. (1998). Rare earth elements in soil and in soil-grown plants. Plant Soil. 199: 267–273.

Wutscher HK, Perkins RE (1993). Acid extractable rare-earth elements in Florida citrus soils and tREE. Commun. Soil Sci. Plan., 24: 2059-2068.

Xu X, Wang Z (2001). Effects of lanthanum and mixtures of rare earths on ammonium oxidation and mineralization of nitrogen in soil. Eur J Soil Sci., 52: 323 – 329

Zeng Q, Zhu JG, Cheng HL, Xie ZB, Chu HY (2006). Phytotoxicity of lanthanum in rice in haplic acrisols and cambisols. Ecotoxicol. Environ. Saf., 64: 226-233.

Zhang H, Feng J, Zhu WF, Liu C, Xu S, Shao P, Wu D, Yang W, Gu J (2000) Chronic toxicity of rare-earth elements on human beings - Implications of blood biochemical indices in REE-high regions, South Jiangxi. Biol. Trace Elem. Res., 73:1-17.

Zhu W, Xu S, Shao P, Zhang H, Wu D, Yang W, Feng J, Feng L (2005) Investigation on liver function among population in high background of rare earth area in south China. Biol. Trace Elem. Res., 104:1-7.

Zu-Yi C, Xu-Dong Z (2009). Accumulation and toxicity of rare earth elements in liver. Acta Ecology of Domestic Animal, 04. Available at:http://en.cnki.com.cn/Article_en/CJFDTOTAL-JCST200904028.htm