ORIGINAL ARTICLE

Soil-to-Plant Transfer Factors of Rare Earth Elements in Rice (*Oryza sativa* L.)

Factores de transferencia suelo-planta de Elementos Tierras Raras en arroz (*Oryza sativa* L.)

http://opn.to/a/kohQR

María Aurora Mesa-Pérez[I]✉, Oscar Díaz-Rizo[II], Marie J. Tavella[III], David Bagué[III], José Miguel Sánchez-Pérez[III]

[I] Universidad Agraria de La Habana (UNAH), San José de las Lajas, Mayabeque, Cuba.

[II] Instituto Superior de Tecnologías y Ciencias Aplicadas, Universidad de La Habana (InSTEC-UH), Plaza, La Habana, Cuba.

[III] CNRS-Laboratoire d'Ecologie Fonctionnel et Environnemental. Université Toulouse 3, France.

ABSTRACT. The present study describes the distribution and bioaccumulation of rare earth elements (REEs) in rice plants grown in San Pedro farm, located in San José de las Lajas Municipality, Mayabeque Province, Cuba. The results indicate that accumulation of REEs in different parts of plants follows the order: root>leaf>husk>grain. The transfer factor (TF) values of REEs in rice were determined, confirming that REE content in rice grains, roots, leaves and husks do not attempt on their use for human consumption and animal food, respectively.

Keywords: Rare earth elements (REEs), soils, rice (Oryza sativa L.), transfer factors.

RESUMEN. El presente estudio describe la distribución y bioacumulación de Elementos Tierras Raras (ETRs) en plantas de arroz provenientes de la finca San Pedro, ubicada en el municipio de San José de la Lajas, provincia de Mayabeque. Los resultados indican que la acumulación de los ETRs en las diferentes partes de la planta, siguen el comportamiento: raíz>hoja>cáscara>grano. Se determinan los valores del Factor de Transferencia (FT) de ETRs in arroz, confirmando que el contenido de ETRs en los granos de arroz, raíces, horas y cáscaras del grano no atentan contra su empleo como consumo humano y alimento animal, respectivamente.

Palabras claves: Elementos Tierras Raras (ETRs), suelos, arroz (Oryza sativa L.), factores de transferencia.

✉ Autor para correspondencia: *María Aurora Mesa-Pérez*. E-mail: mariaa@unah.edu.cu
Received: 18/06/2017
Approved: 14/03/2018

INTRODUCTION

Rare earth elements (REEs) are a group of 15 elements of which only promethium (Pm) does not naturally exist in the Earth's crust (Kabata-Pendias, 2001). From a geochemical perspective, REEs are not particularly rare. In fact, they are as abundant as Cu, Pb, and Zn in the average crust sample. Furthermore, they have higher concentrations than Sn, Co, Ag, and Hg (Wang *et al.*, 2004). REEs are usually divided into two sub-groups: (1) from lanthanum to samarium (with lower atomic numbers and masses), commonly referred to as light rare earth elements (LREEs); and (2) from europium to lutetium (with higher atomic numbers and masses), referred to as heavy rare earth elements (HREEs).

REEs have similar chemical and physical properties and tend to naturally coexist, which explains their similar behaviour in the environment (Hu *et al.*, 2006). REEs have been characterized neither as essential elements for life nor as strongly toxic elements in the environment (Hu *et al.*, 2006; Laveuf and Cornu, 2009). Although there is no report on incidents of human poisoning through food chain (Liu *et al.*, 2013), potential concerns regarding effects of continuous exposure to low levels of REEs on human health have been arising because they are accumulated in blood, brain and bone after entering the human body (d'Aquino *et al.*, 2009). Previous studies have found that high exposure levels of REEs may be related to health problems such as liver function decline (Zhu *et al.*, 2005). In addition, occupational and environmental exposure to REEs can pose health risk to human body (Sabbioni *et al.*, 1982), and little information is so far available about the dose intake and potential health effects of exposure to REEs on human due to food consumption.

Rice is the main garnish and Zinc source in the Cuban diet (Diaz *et al.*, 2013), with the population consuming, in average, around 200 grams per day. For that reason, rice is cultivated along the country in extensive and small areas. On the other hand, after rice harvest and processing for human consumption, the residual parts of the plant (husk, leaves, roots, etc.) are used for farm animal food. The REE content in rice grain is reported only in a few studies (Uchida *et al.*, 2007; Rogan *et al.*, 2012). However, information about the REE translocation to other part of the rice plant is scarce. In this context, the main objectives of the present research are: (1) - to estimate the content and distribution patterns of REEs in the soil and rice crops; and (2) - to assess the mobility and bioavailability characteristics of REEs in soil samples.

METHODS

Rice plants (*Oryza sativa* L., IACuba-15 variety) and soil samples were collected in the same journey during harvesting time in 2013 from 10 sampling sites (1 m^2 each) across San Pedro farm (N 22º 55´53.62´´ y O 82º 2´56.48´´), located in the San José de las Lajas Municipality, Mayabeque Province, Cuba (Figure 1). All plant samples (n=100) were divided into grain (fruit), leaf and root. Samples were stored in plastic bags and subsequently introduced in cold boxes in order to keep the humidity conditions stable during their transport to the laboratory.

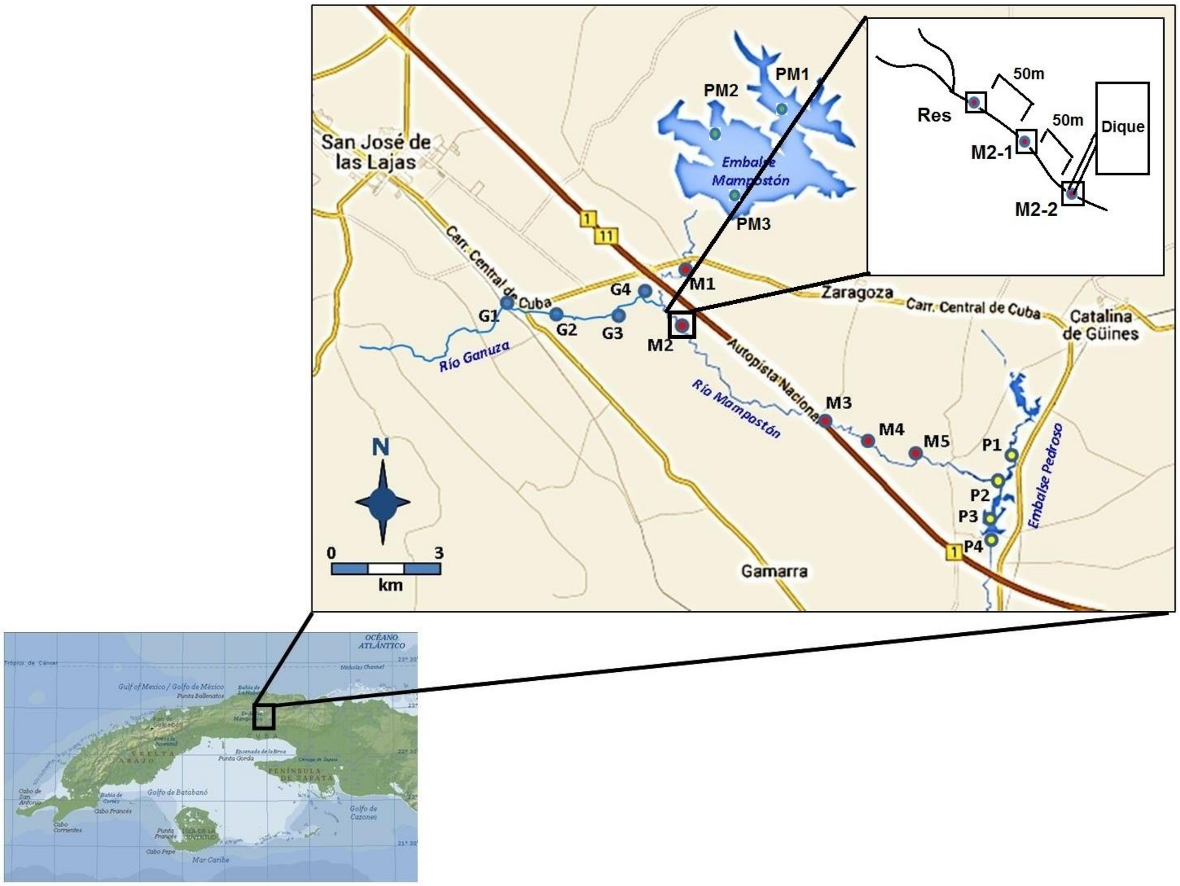

FIGURE 1. Geographical location of San Pedro farm. Source: Woogle Earth (http://www.googlearth.com)

In the laboratory, collected plant parts were carefully washed twice with distilled water. The composite samples were dried at 60 ºC for 48 h, afterwards, grains were polished and separated in white grain and husk. Grains, husk, leaves and roots were sub-sampled in smaller portions, and macerated within an agate mortar, periodically adding liquid nitrogen to enhance the grinding process.

Soil samples were dried at 60 ºC and portioned in three subsamples. Large rock debris; mollusc skeletons and organic debris were removed before sieving. Fraction smaller than 1 mm was sieve to obtain a fine fraction (<63 µm). The subsamples were newly dried at 60 ºC before the experiments.

Pseudototal content of REE was extracted by biacid digestion (HNO_3: HCl) in a ratio of 2: 1 and H_2O_2. The temperature during digestion was 55 ºC - 80 ºC for 3 hours in a Digiprep (Laboratoire d'Ecologie Fonctionnel et Environnemental, Université Toulouse 3. France). Reading was performed by ICPMS Agilent Technologies 7500 CE and HR-ICP-MS Thermo Scientific Element XR at the Observatoire Midi-Pyrénées, Toulouse, France. An $^{115}In/^{187}Re$ internal standard of a known concentration (2.0325 µg.L^{-1}) was added to all the samples, and four quality control samples were introduced following every eight samples to correct for any analyser deviation (Aries *et al.*, 2000). All the determined concentration values were within the detection and quantification limits of the equipment (50 pg.g^{-1}).

Interpretation data was done by normalization with average of Upper Continental Crust (UCC) (Wedepohl, 1995) following the procedure established by Migaszewski y Gałuszka, (2015).

Soil-to-plant transfer is one of the key components of human exposure to REEs that seep into food production. To investigate the transfer values of REEs from soils to crops, the TFs were calculated as follows (Cui *et al.*, 2004):

$$TF = C_{rice} / C_{soil} \quad (1)$$

where C_{rice} and C_{soil} represent REE concentrations in the rice crops and soils, respectively, where the crops are measured on a dry weight basis. In this study, we used the mean concentration values of REEs determined as:

$$C_{rice} = C_{root}+C_{leaf}+C_{grain}+C_{husk} \quad (2)$$

RESULTS AND DISCUSSION

The concentrations of REEs in the studied soils are presented in Table 1. For comparison, they are presented alongside the concentrations of REEs in the upper continental crust (Wedepohl, 1995). The mean REE levels in the soil were slightly higher than the measured mean concentrations of REE in the average upper continental crust. LREEs (La–Sm) accounted for 84.4% of the total REE content in the investigated soils, which is in agreement with the report of Taylor and McLennan (1995), indicating that LREEs are usually more abundant in soils than HREEs, just as they are in the earth's crust.

The upper continental crust normalized patterns show a characteristic pattern of handsaw (Migaszewski and Gałuszka, 2015) of the studied soil (Figure 2, left) did not differ appreciably and revealed a similar REE pattern of studied farm soils to REE concentrations in the average upper continental crust (Wedepohl, 1995) and in soils from different Cuban zones as Piojillo (Rizo and Herrera, 1997), Cayajabos (Montero-Cabrera *et al.*, 2000), La Corea (Blanco-Quintero *et al.*, 2011) and Zaza (Deschamps *et al.*, 2012). That result is the evidence of a lithological contribution of REE in this area, without anthropogenic intervention in that sense.

REE concentrations in rice organs and transfer factors are also reported in Table 1. The rice grain showed the lowest REE content with very significant correlation ($\rho<0.01$) with REE concentration in leaves ($r^2=0.81$) and husk ($r^2=0.80$). Only REE content in roots showed a very significant correlation with REE concentration in soil ($r^2=0.99$).

The UCC normalized patterns of REE in roots (Figure 2, right) are similar to normalized soil patterns, while considerable differ with grain, husk and leaf REE patterns. The concentration of REEs in plants is extremely variable and dependent on the plant species and its corresponding habitat (Taylor and McLennan, 1995; Laveuf and Cornu, 2009). Different parts of a plant can be ranked in the following order based on their REE content: root>leaf>stem>grain (Li *et al.*, 1998; Xu *et al.*, 2002). REE concentrations in roots are usually considerably higher than REE concentrations in other plant parts (Li *et al.*, 1998). Thus, REEs can be accumulated and retained by the roots of rice, with only small portions of the REEs reaching other parts of the plant. This fact helps explaining why the concentrations of REEs in studied rice grain samples were very low.

TABLE 1. Average REE Concentrations (± SD) in Soil ($mg.kg^{-1}$) and *Oryza sativa* L. Organs ($mg.kg^{-1}$). Soil-to Plant Transfer Factor (TF) for Rice

REE	**Soil**[a]	**UCC**	***Oryza sativa* L.**				**TF**
			Root[q]	**Grain**[bc]	**Leaf**[b]	**Husk**[c]	
La	23.1 ± 0.4	30	11.1 ± 0.5	0.08 ± 0.04	0.52 ± 0.32	0.49 ± 0.30	0,5
Ce	69.2 ± 2.4	60	28.6 ± 0.6	0.05 ± 0.02	0.54 ± 0.02	0.16 ± 0.09	0,4
Pr	6.7 ± 3.6	6,7	3.2 ± 0.2	0.07 ± 0.04	0.46 ± 0.02	0.20 ± 0.04	0,5
Nd	30.9 ± 3.2	27	13.6 ± 0.1	0.09 ± 0.05	0.29 ± 0.02	0.39 ± 0.05	0,5
Sm	7.0 ± 5.2	5,3	3.2 ± 0.1	0.09 ± 0.05	0.29 ± 0.06	0.09 ± 0.05	0,6
Eu	1.9 ± 2.2	1,3	1.0 ± 0.1	0.34 ± 0.04	0.64 ± 0.02	0.43 ± 0.13	1,35
Gd	9.5 ± 1.5	4	4.4 ± 0.2	0.12 ± 0.08	0.69 ± 0.02	0.59 ± 0.08	0,6
Dy	6.8 ± 4.7	3,8	3.1 ± 0.1	0.18 ± 0.06	0.76 ± 0.05	0.35 ± 0.06	0,7
Ho	1.4 ± 1.9	0,8	0.8 ± 0.2	0.11 ± 0.08	0.32 ± 0.02	0.62 ± 0.08	1,4
Er	3.8 ± 1.3	2,1	1.8 ± 0.1	0.12 ± 0.07	0.46 ± 0.04	0.52 ± 0.07	0,8
Tm	0.5 ± 1.0	0,3	0.5 ± 0.1	0.57 ± 0.16	2.21 ± 0.52	0.44 ± 0.06	7,1
Yb	3.1 ± 1.8	2	1.81 ± 0.5	0.42 ± 0.06	1.31 ± 0.17	0.34 ± 0.07	1,2
Lu	0.45 ± 0.30	0,35	0.41 ± 0.23	1.82 ± 0.02	1.34 ± 0.80	1.84 ± 0.19	12,0
ΣREE	164,4	144	73,3	4,0	10,1	6,7	
ΣLREE	138,7	129	60,6	0,7	2,7	2,0	
ΣHREE	25,6	15	12,7	3,3	7,4	4,7	

a, b, c - Indicates a significant correlation (ρ<0.01).
UCC – Upper continental crust REE concentrations
Source of UCC data taken from Wedepohl (1995).

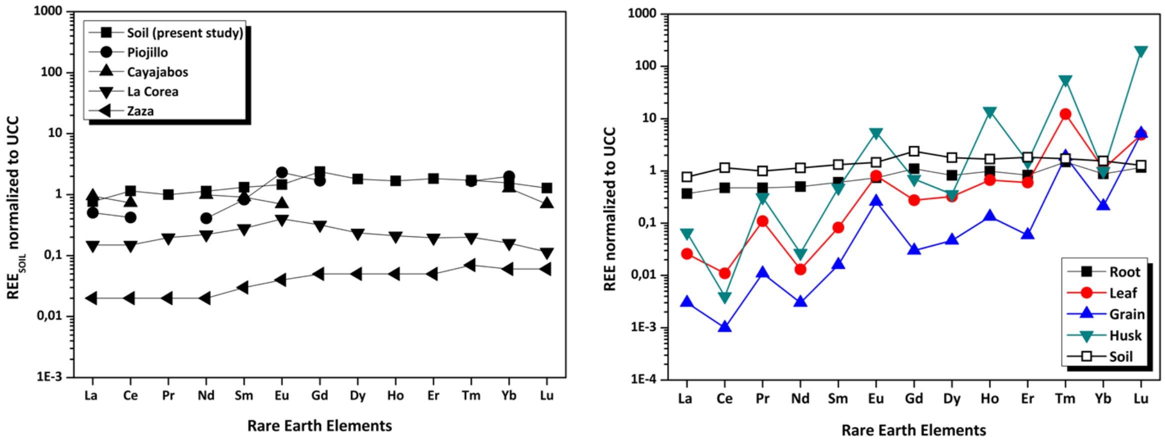

FIGURE 2. UCC normalized patterns of REE content in San Pedro Farm soils and its comparison with REE patterns from other Cuban sites (*left*). UCC normalized patterns of REE in studied rice plant organs and its comparison with soil REE (*right*). Source of UCC data taken from Wedepohl (1995).

The TF values for LREEs in rice were generally very low (Table 1), and they confirmed the weak accumulation of LREEs (La, Ce, Pr, Nd and Sm) by crops. A similar result was reported for Macedonian rice (Rogan *et al.*, 2012). The mean values of TF calculations for La, Ce, Pr, Nd, and Sm were very similar: 0.53 (La), 0.42 (Ce), 0.58 (Pr), 0.46 (Nd), and 0.57 (Sm). Such values may indicate similar fractionation events of these elements in the soil–rice system of the farms studied. On the other hand, according to the obtained TF, rice plant is a good HREE accumulator from soil, principally, in roots. However, the HREE content in rice plant is around the 30% of the total REE content present in rice plant. Then, HREE content in rice plant must not be a problem for use in human nutrition (grain) and the normal rice production wastes (plant roots, leaves and grain husk) for animal food.

CONCLUSIONS

The concentrations of REEs in soil samples of San Pedro Farm are associated with the contribution to soil formation of the rocks lithology prevailing in the area. LREEs (La–Sm) accounted for 84.4% of the total REE content in the investigated soils. The absolute concentrations of REEs in polished rice samples of the farm studied were 40 times lower than those detected in the soils. Additionally, REEs could be accumulated and retained by the roots, and only a small portion of the REEs reached the higher parts (grains) of rice plants. The TF values of REEs in rice were also very low, confirming weak accumulation of LREEs (La, Ce, Pr, Nd, and Sm) by rice crops. The REE content in rice roots, leaves, grain and husk do not attempt on their use for human and animal food.

REFERENCES

ARIES, S.; VALLADON, M.; POLVÉ, M.; DUPRÉ, B.: "A Routine Method for Oxide and Hydroxide Interference Corrections in ICP-MS Chemical Analysis of Environmental and Geological Samples", *Geostandards Newsletter*, 24(1): 19-31, 1 de junio de 2000, ISSN: 1751-908X, DOI: 10.1111/j.1751-908X.2000.tb00583.x.

BLANCO-QUINTERO, I.F.; ROJAS-AGRAMONTE, Y.; GARCÍA-CASCO, A.; KRÖNER, A.; MERTZ, D.F.; LÁZARO, C.; BLANCO-MORENO, J.; RENNE, P.R.: "Timing of subduction and exhumation in a subduction channel: Evidence from slab melts from La Corea Mélange (eastern Cuba)", *Lithos*, 127(1): 86-100, 1 de noviembre de 2011, ISSN: 0024-4937, DOI: 10.1016/j.lithos.2011.08.009.

CUI, Y.-J.; ZHU, Y.-G.; ZHAI, R.-H.; CHEN, D.-Y.; HUANG, Y.-Z.; QIU, Y.; LIANG, J.-Z.: "Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China", *Environment International*, 30(6): 785-791, 1 de agosto de 2004, ISSN: 0160-4120, DOI: 10.1016/j.envint.2004.01.003.

D'AQUINO, L.; DE PINTO, M.C.; NARDI, L.; MORGANA, M.; TOMMASI, F.: "Effect of some light rare earth elements on seed germination, seedling growth and antioxidant metabolism in *Triticum durum*", *Chemosphere*, 75(7): 900-905, 1 de mayo de 2009, ISSN: 0045-6535, DOI: 10.1016/j.chemosphere.2009.01.026.

DESCHAMPS, F.; GODARD, M.; GUILLOT, S.; CHAUVEL, C.; ANDREANI, M.; HATTORI, K.; WUNDER, B.; FRANCE, L.: "Behavior of fluid-mobile elements in serpentines from abyssal to subduction environments: Examples from Cuba and Dominican Republic", *Chemical Geology*, 312: 93-117, 18 de junio de 2012, ISSN: 0009-2541, DOI: 10.1016/j.chemgeo.2012.04.009.

DIAZ, R.O.; OLIVARES, S.; DENIS, A.O.; LIMA, C.L.; D´ALESSANDRO, R.K.; ARADO, L.J.O.: "Bioaccumulation of zinc in crops and its contribution to Zn intake by Cuban population", *Nucleus*, (54): 8-11, 2013, ISSN: 0864-084X.

HU, Z.; HANEKLAUS, S.; SPAROVEK, G.; SCHNUG, E.: "Rare Earth Elements in Soils", *Communications in Soil Science and Plant Analysis*, 37(9-10): 1381-1420, 1 de junio de 2006, ISSN: 0010-3624, DOI: 10.1080/00103620600628680.

KABATA-PENDIAS, A.: *Trace Elements in Soils and Plants*, *[en línea]*, Ed. CRC Press, 3.ª ed., Boca Raton, 436 p., Google-Books-ID: Nowwb0xl9fYC, 2001, ISBN: 978-1-4200-3990-0, *Disponible en: https://books.google.com.cu/books?id=Nowwb0xl9fYC, [Consulta: 7 de septiembre de 2016]*.

LAVEUF, C.; CORNU, S.: "A review on the potentiality of Rare Earth Elements to trace pedogenetic processes", *Geoderma*, 154(1): 1-12, 15 de diciembre de 2009, ISSN: 0016-7061, DOI: 10.1016/j.geoderma.2009.10.002.

LI, F.; SHAN, X.; ZHANG, T.; ZHANG, S.: "Evaluation of plant availability of rare earth elements in soils by chemical fractionation and multiple regression analysis", *Environmental Pollution*, 102(2): 269-277, 1 de agosto de 1998, ISSN: 0269-7491, DOI: 10.1016/S0269-7491(98)00063-3.

LIU, D.; WANG, X.; ZHANG, X.; GAO, Z.: "Effects of lanthanum on growth and accumulation in roots of rice seedlings", *Plant, Soil and Environment*, 59(5): 196-200, 2013, ISSN: 1214-1178.

MIGASZEWSKI, Z.M.; GAŁUSZKA, A.: "The Characteristics, Occurrence, and Geochemical Behavior of Rare Earth Elements in the Environment: A Review", *Critical Reviews in Environmental Science and Technology*, 45(5): 429-471, 4 de marzo de 2015, ISSN: 1064-3389, DOI: 10.1080/10643389.2013.866622.

MONTERO-CABRERA, M.E.; HERRERA-HERNÁNDEZ, H.; HERRERA-PERAZA, E.; RODRÍGUEZ-MARTÍNEZ, N.; LÓPEZ-REYES, M.C.: "Instrumental neutron activation analysis of rocks from Cayajabos petroleum ore", *Applied Radiation and Isotopes*, 52(1): 143-146, 1 de enero de 2000, ISSN: 0969-8043, DOI: 10.1016/S0969-8043(99)00119-0.

RIZO, O.; HERRERA, P.E.: "Multi-elemental characterization of Cuban natural zeolites", *Journal of Radioanalytical and Nuclear Chemistry*, 221(1-2): 255-258, 17 de julio de 1997, ISSN: 0236-5731, DOI: 10.1007/BF02035282.

ROGAN, Š.N.; DOLENEC, T.; SERAFIMOVSKI, T.; DOLENEC, M.; VRHOVNIK, P.: "Geochemical characteristics of rare earth elements (REEs) in the paddy soil and rice (*Oryza sativa* L.) system of Kočani Field, Republic of Macedonia", *Geoderma*, 183: 1-11, 1 de agosto de 2012, ISSN: 0016-7061, DOI: 10.1016/j.geoderma.2012.03.009.

SABBIONI, E.; PIETRA, R.; GAGLIONE, P.; VOCATURO, G.; COLOMBO, F.; ZANONI, M.; RODI, F.: "Long-term occupational risk of rare-earth pneumoconiosis A case report as investigated by neutron activation analysis", *Science of The Total Environment*, 26(1): 19-32, 1 de diciembre de 1982, ISSN: 0048-9697, DOI: 10.1016/0048-9697(82)90093-6.

TAYLOR, S.R.; MCLENNAN, S.M.: "The geochemical evolution of the continental crust", *Reviews of Geophysics*, 33(2): 241-265, 1 de mayo de 1995, ISSN: 1944-9208, DOI: 10.1029/95RG00262.

UCHIDA, S.; TAGAMI, K.; HIRAI, I.: "Soil-to-Plant Transfer Factors of Stable Elements and Naturally Occurring Radionuclides: (2) Rice Collected in Japan", *Journal of Nuclear Science and Technology*, 44(5): 779-790, 1 de mayo de 2007, ISSN: 0022-3131, DOI: 10.1080/18811248.2007.9711867.

WANG, Y.; WANG, J.; WANG, L.; WANG, Y.; TU, C.: "REE Characteristics of the Kalatongke Cu-Ni Deposit, Xinjiang, China", *Acta Geologica Sinica*, 78(2): 396-403, 1 de abril de 2004, ISSN: 1755-6724, DOI: 10.1111/j.1755-6724.2004.tb00146.x.

WEDEPOHL, H.K.: "The composition of the continental crust", *Geochimica et Cosmochimica Acta*, 59(7): 1217-1232, 1 de abril de 1995, ISSN: 0016-7037, DOI: 10.1016/0016-7037(95)00038-2.

XU, X.; ZHU, W.; WANG, Z.; WITKAMP, G.-J.: "Distributions of rare earths and heavy metals in field-grown maize after application of rare earth-containing fertilizer", *Science of The Total Environment*, 293(1): 97-105, 3 de julio de 2002, ISSN: 0048-9697, DOI: 10.1016/S0048-9697(01)01150-0.

ZHU, W.; XU, S.; SHAO, P.; ZHANG, H.; WU, D.; YANG, W.; FENG, J.; FENG, L.: "Investigation on liver function among population in high background of rare earth area in South China", *Biological Trace Element Research*, 104(1): 1-7, 1 de abril de 2005, ISSN: 0163-4984, 1559-0720, DOI: 10.1385/BTER:104:1:001.

The mention of commercial equipment marks, instruments or specific materials obeys identification purposes, there is not any promotional commitment related to them, neither for the authors nor for the editor.