Sustentare

Periódico da Universidade Vale do Rio Verde
ISSN: 2526-690X
v. 4 | n. 1 | 2020

ARTICLE

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RARE EARTH ELEMENTS: WHAT ARE THEY, WHAT ARE THEY AND WHAT ARE THEIR ENVIRONMENTAL EFFECTS?

Abstract: The rare earth elements (REE) has received great importance in recent years and, consequently, are the focus of research in several areas. This fact is due to its great potential and essentiality in industrial activity, mainly in the case of high technology. Also, agriculture receives REE, directly or indirectly, via phosphate fertilization that has been accumulating in the environment. Therefore, there is a current concern in terms of applied levels, as well as environmental effects, both for plants and humans. Reference concentrations for these elements have not yet been defined since their effects have also not been fully elucidated. This review aims to show the history, use, current panorama, and the stage of research related to the effects of REE in different species and their level of emergent contamination.

Keywords: Cerium. Emerging pollutant. Lanthanum. Phosphate fertilizers.

ELEMENTOS TERRAS RARAS: O QUE SÃO, PARA QUE SERVEM E QUAIS SEUS EFEITOS AMBIENTAIS?

Resumo: Os elementos terras raras (ETR) tem recebido grande importância nos últimos anos e, consequentemente, são foco de pesquisas em diversas áreas. Tal fato se deve ao seu grande potencial e essencialidade na atividade industrial, principalmente em se tratando de alta tecnologia. Além disso, a agricultura também recebe ETR, direta ou indiretamente, via fertilização fosfatada e que vêm se acumulando no ambiente. Diante disso, existe a preocupação atual em se tratando dos teores aplicados, bem como os efeitos ambientais, tanto para os vegetais quanto para o ser humano. Concentrações de referência para estes elementos ainda não foram definidas, uma vez que seus efeitos também não foram totalmente elucidados. Esta revisão tem por objetivo mostrar o histórico, utilização, panorama atual e o estágio das pesquisas relacionadas aos efeitos de ETR em diferentes espécies e seu nível de contaminação emergente.

Palavras-chave: Cério. Poluente emergente. Fertilizantes fosfatados. Lantânio.

Recebido em: 21/05/2020 - Aprovado em: 15/06/2020 - Disponibilizado em: 30/07/2020

INTRODUCTION

The Rare Earth Elements (REE) are a group of elements with successive atomic numbers from 57 (lanthanum) to 71 (lutetium) along with yttrium (39) and scandium (21), which are recognized by the International Union of Pure and Applied Chemistry (IUPAC) due to the similar chemical, toxicological behavior and are often found in the same mineral origin. However, instead of what the name might refer, the REE are not rare in nature, since their average content in the earth's crust is approximately 0.015%, as well as copper, lead and zinc (RAMOS et al., 2016 a).

The REE was called “industrial vitamins" and "innovative materials" due to its role in industrial development (RIM, 2016). REEs are associated with the sectors of high technology, electronics, military, "green energy technologies" and communication technology (PANDA et al, 2014). The use of these elements is essential for the production of magnets, electromechanical devices, screen displays, glass, lenses, laser, microwave devices, ceramics, photographic, as well as X-rays and magnetic resonance, including chemicals, transport, health care and aviation (KHAN et al., 2011).

In addition to these uses, China was the first country to apply REE directly via foliar fertilizers in crops and it is also the main country to supply REE, controlling over 90% of the global market. Over the past thirty years, fertilizers containing REE have been widely studied and applied in agriculture to improve crop yield and quality with gains ranging from 5% to 15% crop yield and quality with gains ranging from 5% to 15% for various species and under different soil and nutrient conditions and under different soil and nutrient conditions (HU et al., 2004). Nevertheless, in Brazil, they are applied indirectly via agricultural phosphogypsum and, mainly, through phosphate fertilizers (RAMOS et al., 2016b).

In recent years, REE fertilizers have been widely studied and applied in agriculture and livestock to increase yield and improve quality due to their specific properties (CARPENTER et al., 2015). Also, large-scale resource exploration activities have resulted in a substantial increase in the levels of soil and water contamination in the mining area (MAO et al., 2010). The high use of fertilizers, as well as high-tech products, has been increasing the levels of REE in the environment and in China, the high concentration of REE has already been observed in soils adjacent to agricultural areas with intensive use of enriched fertilizers. Huang et al. (2007) estimated that the extraction rate was 119,000 tons in 2005 in China. Thus, it is expected that rare earth elements will become emerging pollutants. The validity and possible mechanism behind this effect are still unknown, but as REE they are considered non-essential elements for plants and other organisms.

Although several beneficial effects of REE on plants have been reported in the literature, due to the stimulation of these elements in the absorption of nutrients, or even by the increase in chlorophyll synthesis (XU et al., 2002), these elements have not yet been defined as belonging to none of the existing groups in plant mineral nutrition (essential or beneficial). In vegetables, REE endocytosis in cells can be one of the main factors responsible for its effects (WANG et al., 2014). Besides, it is believed that the REE protect plants against diseases, stresses such as drought, cold, acid rain, and heavy metals and lead to increased growth and grain production (HU et al., 2004). Due to the dubious classification, it is necessary to exercise caution when introducing them into the ecosystem, either intentionally or involuntarily, since they are liable to bioaccumulate if transferred from the soil to living organisms and water bodies (RAMOS et al., 2016a).

The excess presence of REE can result in serious consequences for ecosystems and human health since the accumulation of effects on organisms remain fragmented and inconsistent. Compared to extensive research on other metals (Cu, Zn, Ni, Cd, and Pb), only a few publications report REE ecotoxicities (HERRMANN et al., 2016). Gonzalez et al. (2015) identified the toxicity of Ce, Gd, and Lu for a variety of aquatic species. Li et al. (2018) discovered that La was toxic to vertebrates. However, the direct effects of these elements on the plant structure and, consequently, their effect on the food chain are not known. Since Brazil is one of the largest producers of phosphate fertilizers and commodities, which are widely consumed as a basis for food, it is of fundamental importance to know the beneficial/toxic potential of REE. In this regard, the present study aimed to show current and relevant data on the effects of the application of REE in plants, as well as the long-term effect on the environment.

THEORETICAL FRAMEWORK

RARE EARTH ELEMENTS: WHAT ARE THEY?

The Rare Earth Element (REE) became important from the industrial point of view due to their relative scarcity, increasing global demand, in addition to not be replaceable. The set of REE comprises the group of lanthanides with an atomic number between Z = 57 and Z = 71 in the periodic table, also including yttrium and scandium (IUPAC), composing block F of the periodic table. REE has special properties about magnetism, electronics, and luminescence. Such elements are very similar chemically and physically, due to their electronic configuration (oxidation state "+3"), particularly stable, except Ce and Eu (oxidation states "+4" and "+2", respectively) (ALONSO et al., 2012).

These elements are divided into two distinct groups: Light Rare Earth Elements and Heavy Rare Earth Elements. The light ones comprise: La, Ce, Pr, Nd, Pm, and Sm, which are found in greater quantity in the environment, have smaller atomic masses, and also greater solubility and alkalinity (MIGASZEWSKI; GALUSZKA, 2014). On the other hand, the Ministry of Land and Resources of the People's Republic of China refers to samarium, europium, and gadolinium (atomic numbers 62 to 64, respectively) as medium elements (Medium Rare Earth Elements) (LIU et al.,2016). Promethium is the only one that has no natural occurrence, as it is a product of uranium fission (MULLER et al., 2016).

HISTORIC AND DENOMINATION

According to Fernandez (2017), the first reports of the discovery of rare earth elements in Sweden date back to 1787, when Karl Arrhenius, a Swedish army lieutenant, collected the black mineral near the village of Ytterby. Only in 1794, an impure yttrium oxide was isolated from mineral by the Finnish chemist Johann Gadolin, naming it Ytterby, which was later renamed Yttrium by the Swedish chemist Anders Gustav Ekeberg. With the advancement in separation technology, cerium was first prepared in 1827 by the Swedish chemist and mineralogist Carl Mosander. The elements in pure form were prepared for the first time in 1931. However, their uses were modest until the improvements in separation and metallurgical technologies that occurred in the 1950s (US GEOLOGICAL SURVEY, 2013). With the advancement of research and new technologies, it was discovered that these two "lands" (yttrium and cerium) were a complex mixture of many elements.

The REE received the generic denomination “earth" for dealing with metallic oxides and the term “rare" in virtue of these elements occurs associated with minerals, in addition to being difficult to separate. In this way, the REE are not necessarily rare, as they are found in almost all rock formations (TYLER, 2004), referring to an erroneous idea, not being, in fact, scarce, given their relative abundance in the earth's crust (15th most abundant group). As an example, the element thulium (0.5 mg kg-1) and lutetium (0.8 mg kg-1), which are the least abundant in the earth's crust, are more abundant than silver (0.07 mg kg-1) and bismuth (0.008 mg kg-1) (MARTINS; ISOLANI, 2005). We can affirm then that the group receives this name because these elements are distributed and the concentration of it in minerals is low, where the majority of the deposits contain less than 1% of REE and not exceeding 9%. Besides that, the extraction and processing are difficult and costly, due in part to its chemical similarities already mentioned and the majority of these elements will not be extracted as primary products, but obtained as by-products.

PRODUCTION, CONSUMPTION AND CONTAMINATION

There are approximately 34 countries in the world with reserves for REE mineral exploration (CHEN, 2011). According to the US Geological Survey (USGS) Commodity Mineral (2016), REE reserves worldwide are estimated at 130 million tons. China (approximately 55 million tonnes) and Brazil (approximately 22 million tonnes) have large reserves, corresponding to 42.3% and 16.9% of the total worldwide, respectively, followed by Australia (approximately 3.2 million tons) (JORJANI; SHAHBAZI, 2012; FERNANDEZ, 2017). Regarding production, the USGS Mineral Commodity showed that, of 124 thousand tons produced in 2015, China contributed with 87.5%, followed by Australia (8.3%), United States (3.4%), Russia (2.1%), Thailand (1.7%) and Malaysia (0.2%). In addition to the largest producer, China leads consumption by approximately 60% in 2015 (LAURENT, 2015). China's Rare Earth Industry Association estimates that China's REE consumption will still increase from 98,000 tons in 2015 to 149,000 tons in 2020 (USGS, 2016). It should be noted that, despite having the second-largest reserve in the world, Brazil does not correspond to this position, in production and consumption.

REEs are present daily in many technological applications, such as wind generators, batteries for hybrid vehicles, cell phone and TV displays, magnets, medical equipment, among other applications making their demand continue to rise (TYLER, 2004). n addition, illegal mining and trafficking of REE are widespread problems in China, and this monopoly has raised the prices of these elements and raised concerns that may affect its reserves and supply (LIU et al., 2016; MANCHERI, 2015). During 2001 - 2015, Japan's average consumption reached 148.5 kg per 1000 inhabitants, followed by the USA with 50.4 kg per 1000 inhabitants and China with 48.1 kg per 1000 inhabitants. Over the period 1972-2010, the average prices of bastnasite and monazite per kilo in 2015 were USD 5.7 and 1.4, respectively (FERNANDEZ, 2017).

In China, there is the commercialization of fertilizers enriched with REE, and several studies showing productivity gains in several plants and animal species. In that country, fertilizers containing REE are composed of nitrates, chlorides and NPK mixture: 25-28% of lanthanum oxide (La_2O_3), 49-51% of cerium dioxide (CeO_2) and 15-17% of oxide-neodymium (Nd_2O_3) (XIONG, 1995). There are three types of fertilizers more widespread: 1) East: nitrates; 2) Nongle: chloride and nitrogen oxides; and, 3) Sea: complex with amino acids (El RAMADY, 2010). In 1986, Changle was registered as the first commercial fertilizer enriched with REE in China. Changle and Nongle were generally recommended at doses of 400-700 g ha^{-1}, dissolved in water. In subsequent years, other fertilizers were used in the form of ammonium bicarbonate compound (GUO, 1995), where the Chinese fertilizer industry was able to produce a total of 5 million tons of ammonium carbonate fertilizers to meet the needs of 6.68 million hectares of agricultural land.

GEOCHEMISTRY OF THE RARE EARTH ELEMENTS

There is a relatively low number of investigations on REE, compared to other groups of elements, in many environmental aspects (TYLER, 2004). This is due, initially to analytical problems, both the lack of adequate equipment and the lack of reference materials (CAO et al., 2000). However, the increase in production, associated with the demand and increased concentration in fertilizers/soil has boosted the advancement and development of new technologies. Regarding quantification methods, inductively coupled plasma mass spectrometry (ICP-MS), has been used effectively to measure the content of individual rare earth elements in biological and environmental samples (XU et al., 2003).

REEs are widely used in petrology and sedimentology for geochemical tracking, characterized by natural processes or in environmental studies as indicators of sources of geogenic or anthropogenic pollution. The content of REE naturally found in soils depends basically on the source material, as well as on geochemical and biological processes that occur in it. The soils originated from igneous rocks, shale and sandstone, tend to contain more REE when compared to the others, with bastnaesite being the most important REE deposit in the world (RAMOS et al., 2016 b).

One of the most relevant minerals as a carrier of rare earth elements is monazite, which is found in igneous rocks explored for the production of phosphate fertilizers. In this way, the phosphate rocks exploited in Brazil may have higher levels of rare earth elements in its chemical composition, this composition is dependent on the locality where the raw material is extracted. Thus, phosphate fertilizers produced in Brazil, especially at the VALE industrial units of Catalão-GO and Araxá-MG, phosphoric acid and by-products such as phosphogypsum can carry large amounts of REE in agricultural systems. In calculations performed by Ramos et al. (2016 b) phosphate fertilizers possibly added 12 thousand tons of Ce to Brazilian soils in 2014, values very close to the number of micronutrients applied in Brazilian agriculture. Although there is almost no large-scale exploration of rare earth minerals in Brazil, the sources are significant and occur mainly in association with carbonate complexes (ANTONIASSI et al., 2015).

REE EFFECTS ON PLANTS

The understanding of the biological function of REE is in its early stages (SKOVRAN & MARTINEZ-GOMEZ, 2015). Although these elements have not yet been classified as essential, beneficial or toxic, several hypotheses have been proposed for the action of the same in the growth and development of plants, both in the metabolic level, cytogenetic and structural, as well as in environmental issue (RAMOS et al., 2016a). So, the mechanisms of assimilation, transport and accumulation in vascular plants are still poorly understood.

Studies on the addition of these elements in fertilizers in an area of 0.5 million there showed an increase in the quality and yield of various species of plants, including cereals, fruit and vegetables, with positive responses in the order of 5 to 15%, resulting from the application of these elements (XIONG, 1995). The reported effects are mainly related to physiological changes such as increased enzyme activity, increased chlorophyll content and photosynthetic rate, increased resistance to environmental factors, in addition to synergistic and antagonistic effects on the absorption of nutrients such as N, K and P. The hypotheses that support the beneficial effects of REE on plant metabolism range from stimulating the antioxidant system, absorbing nutrients, fixing nitrogen and CO_2 and enhancing biomass production by increasing the photosynthetic rate, due to the increased rate of electron transport in the photochemical phase of photosynthesis (RAMOS et al., 2016). However, the mechanisms responsible for the influences caused by REE are still unclear.

On the other hand, it was reported that high concentrations of REE decrease significantly the photosynthetic rate and chlorophyll content (CHATURVEDI, GANNAVAPARU; KUMAR, 2014; SHYAM & AERY, 2012). In this case, the REE could enter the plant cells and be deposited in chloroplasts, which may damage its structure, negatively affecting photosynthesis and, consequently, the plant growth (GUO, 2014; WANG et al., 2014). There are also assumptions that these elements would be capable of replacing Ca in the cell wall structure, in the cytoskeleton and organelle membranes, alteration in the size and density of anatomical structures such as stomata, trichomes and tissue thickness; or even, increased mitotic index, abnormalities of the cell cycle that benefit the production of biomass, such as the appearance of binucleated cells (OLIVEIRA et al., 2015). It is also important to report that phytohormone production is affected by the presence of REE and this interaction has been proposed as one of the mechanisms by which these elements can influence plant growth (LUO et al., 2008; WANG et al., 2014).

ENVIRONMENTAL AND HUMAN HEALTH RISKS

Currently, little attention has been given to the ecological aspects related to the presence REE in soils and their possible transfer in the trophic chain (GONZALEZ et al., 2014; PAGANO et al., 2015). Although there are no reports of cases of human poisoning through the food chain, potential concerns about the effects of continued exposure to low levels of REE on human health have arisen because they accumulate in the blood, brain and bones after entering the human body. (CHEN, 2005; CHEN & ZHU, 2008; ZAICHICK et al., 2011). Medical and pharmacological studies have reported an accumulation of these elements over the long term, these elements being accumulated in the lungs, causing cardiac, hepatic, hematological and renal damage, in addition to effects on the gastrointestinal tract, bones, lung and cytogenetics. (HIRANO; SUZUKI, 1996, RIM et al., 2013). Long-term exposure can also be related to health problems such as the decline of hepatic function (ZHU et al., 2005). Despite this, the current information is not sufficient to determine safe human exposure levels (USEPA, 2009).

Although these data are useful to assess the potential risks of REE for humans, only in specific cases, there will be direct exposure to salts/oxides of these elements. In most cases, the main routes of exposure will be the ingestion of contaminated food, water and soil, as well as contact and inhalation of vapors and particulate materials. (USEPA, 2012). Therefore, it is necessary to know the actual doses, which the organisms are exposed. For better REE risk estimates, it would be necessary to carry out of bioaccessibility studies, such as those implemented by Smith et al. (2000) who evaluated the bioaccessibility content (physiological based extraction test) of La, Ce and Nd in soil samples (ground soils) and soils deliberately consumed, such as termite nest and traditional herb soils, in the Mukono district (Uganda). Each scenario must be specifically assessed, considering the intrinsic variability of each environment under consideration, as well as the objectives of the assessment, target organisms, among others.

The REE excess presence in soils can result in serious consequences for ecosystems, agricultural productivity and human health. Under these circumstances, the REE in soil and water is released and potentially enters the human body through several exposure routes, especially food intake. More attention should be paid to the effects of continuous exposure to low levels of REE in children. Zhuang and collaborators in 2017, investigated the concentrations of rare earth elements in vegetables and assessed the risk to human health by consumption of vegetables, collecting 301 samples of plants of the mining area and control area in Shandong. The health risk assessment showed that the estimated daily doses (0.69 mg kg $^{-1}$ and 0.28 mg kg $^{-1}$ for mining and control areas, respectively) of REE through vegetable consumption was significantly lower than than the acceptable daily intake (70 mg kg^{-1}). Therefore, it is necessary to investigate their levels of concentration in the daily diet of vegetables, grains and meat to assess the potential risk of REE for human health.

It is known that the toxicity of the REE is variable, depending on the toxicological parameters and target organisms. Also, chemical forms of the REE compounds determine mainly deposition and retention according to the different routes of exposure. These data reinforce the need to evaluate bioaccessible content, particularly when taking into account the great differences found between the different routes of exposure, for example, oral vs intravenous. However, the existence of a limited number of studies on this subject, as well as others involving several important ecological indicators (for example, invertebrates, birds, etc.), reveals the great challenge that researchers still have in generating consistent information to evaluate the real effects on the ecosystem.

Although studies that evaluate the REE effects in the environment may present relevant information to contribute to the ecological assessment of risks, the comparison of existing studies is difficult due to methodological divergences.

FINAL CONSIDERATIONS

The information available in the literature are of fundamental importance in terms of prospecting for effects and the potential use of REE. However, there are still gaps, mainly concerning the concentration for the safe application and what would be considered toxic to living beings, in addition to unraveling the physiological effects that these elements can promote in plants. A clear understanding of the relationship between the amount absorbed and the content of REE in plants, and their effects on vegetables, is essential to elucidate the performance of these elements since from these, they will be carried in the food chain. Thus, further studies are needed to obtain accurate information on the actual effects and doses for the safe use of phosphate fertilizers with REE as well as the exposure time in the vicinity of the mining area. For the use of REE, as occurs in China, its effects on all parts of the food chain, as well as on the environment should be elucidated. That way, issues associated with the production, processing, use of REE and its effects on food production constitute a thriving area of research.

ACKNOWLEDGMENTS

To the Vale Technological Institute (ITV) and the Federal University of Lavras (UFLA) (cooperation agreement ITV / UFLA 020 Vale Terras Raras) for promoting the work based on this review, under the guidance of Dr. Sílvio Junio Ramos and Dr. Cynthia de Oliveira. To CAPES and FAPEMIG for the authors' scholarships.

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