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Application and Effects of Rare Earth Elements in Agricultural Production Systems

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ABSTRACT

Objective: To review the history of rare earths and their practical applications, as well as to identify the effects of some rare earths on crops.

Design/methodology/approach: We performed an exhaustive review of the scientific literature related to the history of rare earth elements (REE), their chemical characteristics, composition in the Earth's crust, and uses in industry, as well as of the effects of the light rare earth elements (LREE) on higher plants. The most relevant articles on the aforementioned topics of interest were then selected, analyzed, and discussed.

Results: In recent years, the industrial and technological use of REE has increased significantly. Their use in the automotive, aeronautical, and space industries, in medicine, in renewable energies, and in electronic and military technology is resulting in the accumulation of these elements in the environment and their bioavailability for crops. Importantly, REE have been reported to have both stimulatory and inhibitory effects on biological systems, including plants.

Limitations on study/implications: While some REE like lanthanum (La) and cerium (Ce) have been extensively studied, others have been scarcely explored and, therefore, little information has been published on them in the international literature.

Findings/conclusions: The use of REE in technology, combined with poor waste management and recycling, cause contamination in soil and water, allowing REE bioavailability in plants. Further studies are needed to identify beneficial effects of REE in the face of biotic or abiotic stress factors.

Keywords: Lanthanides, Biostimulants, phytotoxicity, LREE, HREE.

INTRODUCTION

Rare earth elements (REE) include the 15 lanthanides (elements from atomic number 57 to 61), in addition to scandium (Sc) and yttrium (Y); these have become critical elements today due to their high demand and use in renewable energy techniques, low recycling rates, and possible scarcity in the future [1,2]. Based on their atomic weight, these elements are divided into light rare earths (LREE) and heavy rare earths (HREE) as shown in Table 1. These minerals are widely used, as they are useful in the automotive, aerospace, medical, renewable energy, electronics, and military industries. For the automotive industry alone, in the area of production of electrical units, an increase in demand of 22% (315 Mg of REE) is expected globally for the period 2018 to 2030 [3,4].

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Table 1. Classification and properties of rare earth elements [1].

Element	Symbol	Atomic number	Atomic mass (g mol^{-1})	Oxidation states	Electronegativity (Pauling scale)
Light Rare Earth Elements (LREE)					
Scandium	Sc	21	44.9	+3	1.36
Lanthanum	La	57	138.9	+3	1.10
Cerium	Ce	58	140.1	+3, +4	1.12
Praseodymium	Pr	59	140.9	+3	1.13
Neodymium	Nd	60	144.2	+3	1.14
Promethium	Pm	61	147	+3	1.13
Samarium	Sm	62	150.3	+2, +3	1.17
Europium	Eu	63	151.9	+2	1.2
Heavy Rare Earth Elements (HREE)					
Yttrium	Y	39	88.9	+3	1.22
Gadolinium	Gd	64	157.2	+3	1.2
Terbium	Tb	65	158.9	+3	1.2
Dysprosium	Dy	66	162.5	+3	1.22
Holmium	Ho	67	164.9	+3	1.2
Erbium	Er	68	167.2	+3	1.2
Thulium	Tm	69	168.9	+3	1.25
Ytterbium	Yb	70	173	+2, +3	1.1
Lutetium	Lu	71	174.9	+3	1.2

Contrary to what their name suggests, so-called rare earths are relatively abundant in the Earth's crust. China has the largest REE reserves and therefore has ample market control. Globally, by 2022, REE reserves were estimated at 130 million Mg (Figure 1). Of this volume, China holds about one third with 44 million Mg, followed by Vietnam, Brazil, Russia, the United States, and Australia [5,6]. Since 2019, China has accounted

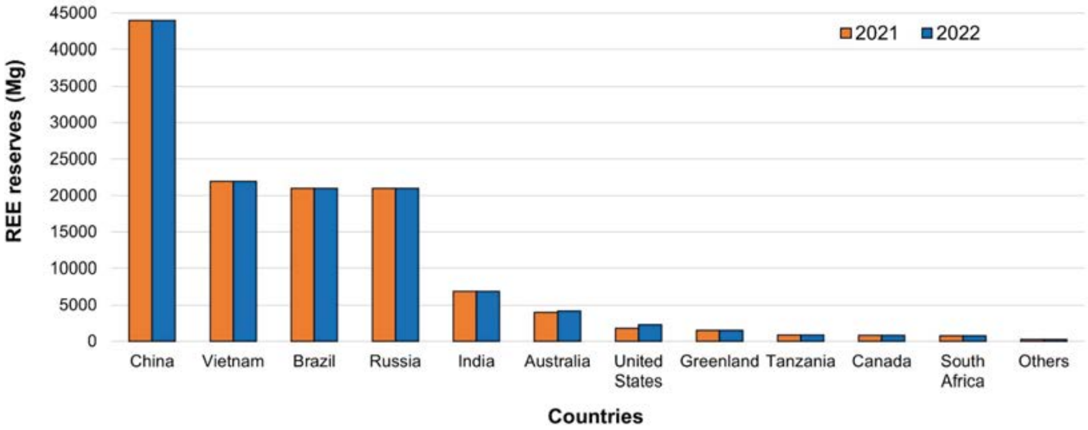

Figure 1. Ranking of countries with the largest reserves of rare earth elements (REE) [5].

for slightly more than 80% of the world production of REE, and by 2022, its share of their extraction and separation of these rose to 210 000 Mg, 190 850 Mg of which were LREE. REE extraction in the United States, Australia, Burma, and Thailand was 43 000, 18 000, 12 000, and 7 100 Mg, respectively [3,6].

REE reserves in North America are estimated to be 3.6 million Mg in the United States and more than 14 million Mg in Canada. REE are mainly extracted from bastnaesite mined in Mountain Pass, CA, and from monazite from the southeastern United States [6]. Mexico has some REE reserves, although there is little or no commercial extraction. For example, the Cerro de Mercado mine in Durango is considered among the main deposits of fluorapatite ore [$Ca_5(PO_4)_3F$], which contains high amounts of Nd, up to 0.45% by weight of neodymium oxide (Nd_2O_3) [7]. Similarly, fluorapatite and some associated minerals can contain up to 3 000 mg Ce kg^{-1}, 2 000 mg La kg^{-1}, and 500 mg Nd kg^{-1}, as well as, Y, Gd, and Pr in concentrations of less than 500 mg kg^{-1} [8].

In Guanajuato, Mexico, the average concentration of some REE in the soil is 103 mg Ce kg^{-1}, 38 mg La kg^{-1} and 41 mg Nd kg^{-1}. For the other REE, concentrations are less than 8 mg kg^{-1}. In water, Ce concentrations range from a few nanograms per liter to 0.5 mg L^{-1}. Elements such as Tb, Ho, Tm, and Lu are found at levels below the detection limit [9]. Even with these data, REE mining is not an economically important activity in Mexico, although their existence makes it necessary to study them for different applications. This paper provides an exhaustive review of historical aspects of rare earths and their practical applications, and also identifies the effects of some rare earth elements on crops.

HISTORY OF THE DISCOVERY OF RARE EARTHS

In 1787, the Swedish chemist Carl Axel Arrhenius (1757-1824) found a dark colored mineral that he named “Ytterby heavy stone” in the village of Ytterby, Sweden [10]. By 1792, the Finnish chemist Johan Gadolin (1760-1852) received a sample of such a mineral from Arrhenius and discovered that 38% of it was a new element he called ytterbia, which was later known as yttria; in 1794, the substance Gadolin was discovered and published with the name of yttrium oxide, and it was considered the first element of the so-called isolated “rare earths” [11].

In 1803, the Swedish chemists Jöns Jacob Berzelius (1779-1848) and Wilhelm Hisinger (1766-1852), as well as the German chemist Martin Heinrich Klaproth (1743-1817), simultaneously analyzed an ore from the Bastnäs iron mine in Sweden. Berzelius and Hisinger called it waxy oxide, while Klaproth called it terre ochroite. Later, Berzelius renamed the compound ceria or cerite, which was eventually changed to “cerium,” after the dwarf planet Ceres [12].

In 1839, the Swedish chemist Carl Gustaf Mosander (1797-1858) showed that ceria was a complex composition of “earths,” from which he separated an oxide he named lanthana, today known as lanthanum [13]. In 1843, Mosander separated yttria and discovered three other compounds, including erbium and terbium, the latter named after Ytterby, Sweden. In 1878, the Swiss chemist Jean Charles Galissard de Marignac (1817-1894) discovered ytterbium by separating it from the rare earth erbia [14].

In 1879, the Swedish chemist Lars Fredrik Nilson discovered scandium by spectral analysis of gadolinite. The name scandium was derived from his country's name, Scandinavia [15]. In the same year, the Swedish chemist Per Teodor Cleve (1840-1905) discovered thulium by obtaining a sample of erbia free of iterbia and scandia, which he dissolved into three constituents: erbia, holmia, and thulia. Thulium was so named because Thule was the ancient name for Scandinavia. In the same year, the Swiss chemists Jacques-Louis Soret (1827-1890) and Marc Delafontaine (1837-1911) studied holmium by spectroscopy. However, it was Cleve who separated it, naming it after Holmia, the Latin name for the city of Stockholm, although all three were credited with the discovery of the element [14].

The Swiss chemist Jean Charles Galissard de Marignac discovered samarium in 1853, and in 1886 he extracted gadolinium, a name he coined in honor of Johan Gadolin, the initiator of rare earth studies. The French chemist Paul Émile Lecoq de Boisbaudran (1838-1912) isolated samarium in 1879 from samarskite earth [16]. In 1885, the Austrian Baron Carl Auer Freiherr von Welsbach (1858-1929) discovered praseodymium and neodymium from the splitting of didymium, which he obtained from residues left over from the extraction of cerium and lanthanum [14].

In 1886, Lecoq de Boisbaudran separated dysprosium from dysprosium oxide dissolved in acid and ammonia. In 1889, the English chemist William Crookes (1832-1919) separated and made the first references to europium, so called in Europe, but it was the French chemist Eugène-Anatole De-marçay (1852-1903) who, in 1901, by crystallization sequence of samarium and magnesium nitrate, isolated europium [18].

The French chemist Georges Urbain (1872-1938) published in 1907 that he had discovered lutetium, named after Lutetia, the ancient name of Paris. In 1908 von Welsbach reported having isolated the same element, calling it cassiopium, a name used in German-speaking countries for some years. Both scientists found it as an impurity of ytterbium [19]. Between 1913 and 1914 the Danish physicist Niels Henrik David Bohr (1885-1962) and the English physicist and chemist Henry Gwyn Jeffreys Moseley (1887-1915) established that the so-called rare earths were composed of 15 elements [20].

In 1947, the American chemists Charles DuBois Coryell (1912-1971), Jacob Akiba Marinsky (1918-2005), and Lawrence Elgin Glendenin (1918-2008) proved the existence of promethium (named after the titan Prometheus) after analyzing the ashes of a nuclear reactor [18]. This concludes the search for rare earth elements, which began in 1787 [10]. The above events are depicted in Figure 2, as an abbreviated timeline.

EFFECTS OF LREE ON CROP PLANTS

Lanthanum (La)

It is a metallic, malleable, ductile, and soft element, found in nature in combination with cerium and other elements such as neodymium or yttrium, forming minerals such as monazite and bastnasite. Regarding its percentage in the Earth's crust, it occupies the twenty-eighth place (0.0032%), its abundance in soil is approximately 32 mg kg^{-1} and its extraction is a challenge for mining [19-24].

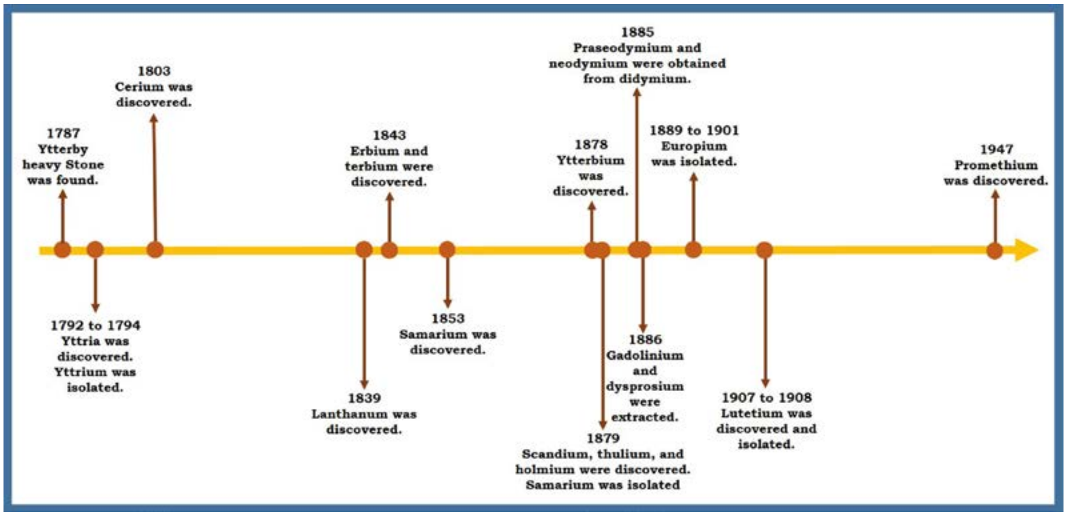

Figure 2. Timeline of the discovery of rare earth elements.

In two varieties of lisianthus (*Eustoma grandiflorum*), Mariachi Blue and Echo Lavanda, the application of lanthanum in the nutrient solution at concentrations of 0, 10, 20, and 30 μM delays the onset of flowering, flower opening, full flowering, and senescence, and only the 10 μM dose increases flowerpot life in both varieties [25]. With the addition of 40 μM La to the preservative solution of 15 varieties of tulip (*Tulipa gesneriana*), higher concentrations of total soluble sugars in petals and total soluble proteins in leaves, increases in fresh weight of stems, and longer vase life were found; it also improves the concentrations of biomolecules [26]. In switchgrass (*Panicum virgatum* L.) seedlings, the addition of La (10 μM), abscisic acid [ABA (10 μM)], and the combination of both (La+ABA) improved metabolic activity and root elongation, and increased leaf chlorophyll content [20].

Cerium (Ce)

Cerium (Ce) is the most abundant REE in the Earth's crust (0.0043%); its concentration in soils ranges from 20 to 68 mg kg^{-1}. It is used in the ceramics and glass industries [19,23,27,28]. Its main source is monazite. The countries with the largest number of Ce mines are China, USA, Brazil, India, Sri Lanka, and Australia [23].

Beneficial effects of Ce have been demonstrated in some crops. For example, in common bean (*Phaseolus vulgaris*), treatments with 50, 100, and 200 mg Ce kg^{-1} increase stomatal conductance; doses with 200 mg Ce kg^{-1} alter the homeostasis of the antioxidant defense system and lipid peroxidation in roots and increase the mineral content of the pods [29]. In tomato (*Solanum lycopersicum*) cv. Bonny Best exposed to doses of 0, 50, and 250 mg Ce kg^{-1}, it increased fruit dry weight and lycopene content, and suppressed wilting caused by *Fusarium* [30]. In maize (*Zea mays*) seedlings treated with Ce (0, 200, 400, 600, 1000, and 2000 mg kg^{-1}) and Cd (0 and 0.5 mg kg^{-1}), it was observed that Ce affects Cd absorption and translocation. In addition, it was found that Ce partially controls the content of B, Mn, Ni, Cu, Zn, Mo, and Fe in roots and shoots, and affects root anatomy [31].

Praseodymium (Pr)

Praseodymium (Pr) is a light metal with high corrosion resistance when exposed to the environment. It ranks 42nd in abundance in the Earth's crust (0.00095%) and has an average concentration of 9.5 mg kg^{-1} in soil. It is obtained from minerals such as monazite and bastnasite [23,24,32-33].

There are few studies on the effects of Pr on plants. In the medicinal plant danshen (*Salvia miltiorrhiza*), doses with 100 μM Pr induced greater root length and improved chlorophyll content, antioxidant enzyme activity, and production of secondary metabolites [34]. In maize (*Zea mays*) cv. Xindan 29, under Cd stress (0, 50, 100, 100, 150, and 200 mg L^{-1}) and treated with 10, 30, and 90 μM Pr per day, Pr improved maize tolerance to Cd, through the regulation of enzymatic activities in the regeneration and biosynthesis pathways of ascorbate and glutathione [35]. In trumpet lily (*Lilium longiflorum*) treated with praseodymium nitrate [$Pr(NO_3)_3$], the activity of peroxidase (POD), catalase (CAT), and four enzymes in the ascorbate-glutathione cycle increased, in addition to soluble sugar and proline content, resulting in better quality and longer vase life [36].

Neodymium (Nd)

With 0.0038% of the total Earth's crust (38 mg kg^{-1}), Nd ranks 27th among the elements contained in it [37]. Although Nd is not naturally free in the environment, electronic, automotive, and medical waste containing Nd can contaminate soil and water, affecting the environment and making this REE bioavailable.

This element has different effects on plant morphology, physiology, and biochemistry, and these depend on the form of application, phenological stage, and edaphoclimatic conditions in which the plant develops [38]. For example, in sicklepod (*Cassia obtusifolia*) seeds treated with 3 mg Nd L^{-1}, improvements in germination and seedling growth were observed [39]. In seedlings of lettuce (*Lactuca sativa*) cv. Rhodenas, Nd (40 and 60 μM) increased plant height, as well as leaf and root length [40]. Likewise, in lettuce cv. Ruby Sky, doses of 2,855 and 5,770 mg Nd L^{-1} increased plant height, leaf area, root volume and whole plant fresh biomass weight, in addition to significantly increasing leaf concentration of N, P, and K [41]. In sugarcane (*Saccharum* spp.) seedlings, the addition of 100 and 150 μM Nd to the nutrient solution improved growth and nutrient concentration [42].

Promethium (Pm)

Promethium (Pm) is an element without stable isotopes, which can be found in the Earth's crust in small quantities (4.5×10-20 mg Pm kg^{-1}). Marketable Pm comes from nuclear reactors and is obtained from fission products of uranium, thorium, and plutonium [23,24,43]. It is required in the phosphor industry, in Liquid Crystal Display (LCD) lamps, in the construction of laser beams, in long-life miniature atomic batteries, and in aperture calipers, the last used especially in the aerospace area [23,43].

Its effect on plants has not been extensively studied due to its low occurrence or bioavailability in soils. In podzols and sierozem soils with a concentration of 0.37 MBq

147Pm kg^{-1}, the accumulation of this element in higher plant tissues behaved as follows: barley grain < wheat grain < pea seeds < potato tubers < radish roots < sugar beet roots, indicating that Pm tends to lodge in lower parts [44].

Samarium (Sm)

Samarium (Sm) is a slightly soft, silver-colored metal that is separated and purified by ion exchange. Its abundance in the Earth's crust is 7.9 mg kg^{-1} and is found mainly in monacite. The main mines of extraction are in the United States, Brazil, India, Sri Lanka, and Australia. Worldwide, 700 Mg of Sm are produced per year [21, 23, 45]. It is used in the technology industry and may be present in some commercial phosphate fertilizers [45]. The bioavailability of Sm depends on the source and chemical characteristics of the soil (pH, texture, and organic matter content). The over-accumulation of Sm causes toxicity in both plants and mammals [45-47]. In wheat (*Triticum aestivum*), the 2 500 μM Sm dose induced a hormetic effect on growth and dry weight increases [48].

With the data presented above, there is evidence that six of the 17 REE exhibit beneficial effects in some crops, in diverse agronomic, physiological, and biochemical attributes that can contribute to increasing quality and yield indicators, as well as improving responses to biotic and abiotic stress factors. The effect of more REE remains to be explored in order to decipher their hormetic curves and determine the application ranges for their best use. The potential offered by these elements is encouraging in the face of the global challenges imposed by increased demand for food for a growing population, in restrictive environments aggravated by global climate change.

CONCLUSIONS AND PROSPECTS

As a consequence of the rise in REE use in various industries, their accumulation levels in the environment have increased. This means that various organisms in ecosystems are exposed to these elements, which makes it necessary to study them and determine their hormetic curves. In this review it has become clear that the REE La, Ce, Pm, Pr, Nd, and Sm can have some beneficial effect on plants, which makes them excellent candidates for the development of technologies that allow their use as inorganic biostimulants. Future research on sources, formulations, doses, frequency of application, and genotypes that show better responses will help to expand their use in improving yield indicators, quality and responses to limiting environmental factors.

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