

Rare Earth Elements in the Soil Environment

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Abstract Rare earth elements (REE) are a homogenous group of 17 chemical elements in the periodic table that are key to many modern industries including chemicals, consumer electronics, clean energy, transportation, health care, aviation, and defense. Moreover, in recent years, they have been used in agriculture. One of the consequences of their worldwide use is the possible increase of their levels in various environmental compartments. This review addresses major topics concerning the study of REE in the soil environment, with special attention to the latest research findings. The main sources of REE to soils, the contents of REE in soils worldwide, and relevant information on the effects of REE to plants were explored. Ecological and human health risk issues related to the presence of REE in soils were also discussed. Although several findings reported positive effects of REE on plant growth, many questions about their biological role remain unanswered. Therefore, studies concerning the actual mechanism of action of these elements on cellular and physiological processes should be further refined. Even more urgent is to unveil their chemical behavior in soils and the ecological and human health risks that might be associated with the widespread use of REE in our modern society.

Keywords Lanthanides · Fertilizers · Bioavailability · Bioaccessibility · Environmental safety · Risk assessment

Introduction

Rare earth elements (REE) are identified by the International Union of Pure and Applied Chemistry (IUPAC) as a group of 17 elements with similar physicochemical characteristics. Of these elements, 15 belong to the group of lanthanides with atomic numbers between $Z = 57$ and $Z = 71$, as follows: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutecium (Lu). Two more elements join them: scandium (Sc, $Z = 21$) and yttrium (Y, $Z = 39$) [1]. The REE are commonly divided into two distinct groups: light (LREE) and heavy (HREE). The LREE are La, Ce, Pr, Nd, Pm, and Sm. They are found in higher amount in the environment, present smaller atomic masses, besides higher solubility and alkalinity. The following elements are part of the HREE group: Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y. These elements have higher atomic masses, smaller solubility, and alkalinity [2]. However there is no absolute definition in the scientific community worldwide to classify each element within the group of LREE or HREE.

Since the first report of rare earth element (REE) detection in apatites of sedimentary and biological origins, as well as in barley, beechwood, and rice and in the leaves of tobacco and grape in 1878 [3], there has been an increasing interest for the study of REE in the soil environment. Yet, our understanding of the biological role of REE is still in its early stages [4], which reinforces the need for continuous research to better understand the environmental effects of REE enrichment of

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soils as a consequence of their increasing use in industrial and agricultural practices.

A survey of the Web of Science database (2015 Jun 14) showed that the scientific literature comprised 1205 references (including 46 patents) on studies of REE in soils using the following keywords: “rare earth elements” AND “soil.” Half of the references (603) were published in the last 6 years (since 2009), and ~56 % of them were concentrated in five countries: China (with ~27 % of the references), USA, France, Japan, and Germany. This survey was further refined by entering the keyword “pollution” (rare earth elements AND soil AND pollution), leading to a subset of 260 references. Again, the great majority of the references (~57 %) were published in recent years (since 2010), and half of them (130) came from China, Japan, Germany, and France. By replacing the third keyword with “plant” (rare earth elements AND soil AND plant), we collected 369 references, and when we added pollution to this last refinement (rare earth elements AND soil AND plant AND pollution), we have recovered only 91 references from the previous search, with ~57 % published since 2010. Lastly, by using a combination of keywords rare earth elements AND soil AND “risk assessment,” we found only 15 references that corresponded to our search criteria.

From the previous information, it is clear that research with REE in soils has been concentrated mostly in the last 5–6 years and only in a few countries. It is also noteworthy that studies with REE in soils with a focus on their effect in plants and in the environment are still limited. Finally, we certainly could conclude that studies focusing on risk assessment of REE in the soil environment are an urgent need, taking into consideration the increasing worldwide use of REE in recent years.

This review was prepared in order to address relevant information (published preferentially in the last 5–6 years) concerning REE in the soil environment, with a focus on the following: (1) the main sources of REE to soils; (2) the major factors affecting the content of REE in soils worldwide; and (3) relevant information on the effects of REE to living systems, with a focus on plant studies and on the need for urgent investigations related to risk assessment of REE in the soil environment (Fig. 1).

Discovery and Occurrence of REE

The history of the discovery of REE is a complex subject full of controversy. In one of the versions, which started in 1787, Carl Axel Arrhenius discovered a heavy black mineral in a trip near the village of Ytterby in the Island of Resarö (east of Stockholm). In 1794, the Finnish professor of chemistry and mineralogy Johan Gadolin analyzed a sample of this mineral provided by Arrhenius and found a new “earth,” naming it Ytterby. Years later, the Swedish chemist Anders Gustav Ekeberg renamed this earth as yttrium. In another version, it is affirmed that the first registration occurred in 1751, when the Swedish chemist Axel

Frederik Cronstedt discovered a heavy rock in the Bastnas mine in Sweden, in which Martin Heinrich Klaproth and Jons Jacob Berzelius, along with Wilhelm Hisinger later in 1803, isolated an earth that they named cerium. Thus, in the beginning of the nineteenth century, two REE were known “yttrium” (discovered in 1794) and “cerium” (discovered in 1803) [5]. As time passed and new technologies were developed, it was found out that these two earths (yttrium and cerium) were a complex mixture of other elements. Currently, the rare earth family consists of 17 transition metals located in group 3 of the periodic table.

The abundance of REE in the earth crust is significant. In contrast with its denomination, the REE are not necessarily rare, because they are found in almost all rock formations [6]. Cerium is the most abundant REE and the 25th most abundant element in earth’s crust [7]. The lanthanides found in smaller concentrations—Lu and Tm—are more abundant in the earth crust than cadmium (Cd) and selenium (Se) [8]. Pm is the only artificial element, which is, it does not occur naturally in earth’s crust [9, 10].

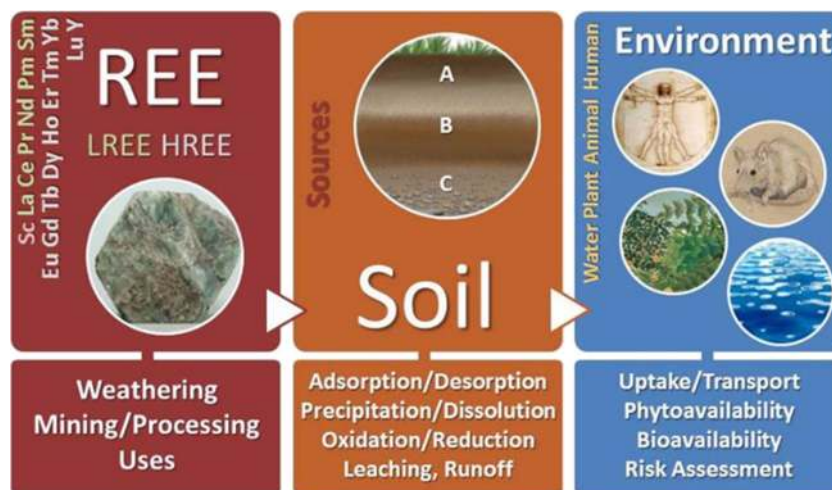
Known reserves of REE (approximately 130 million tons) are extensively distributed worldwide. They occur in 6 European countries, 14 Asian countries, and 10 African countries, as well as in the USA, Canada, Australia, and Brazil [11]. China has the largest reserves (approximately 55 million tons) and appears as the world’s largest REE producer (about 86 % of the production). Brazil is the second country in REE reserves (approximately 22 million tons), followed by Australia, with approximately 3.2 million tons [12].

Characteristics and Uses of REE

The REE are very similar chemically and physically, and this uniformity comes from the nature of their electronic configuration, generally reaching an oxidation state “+3,” particularly stable, and a small but constant reduction in the ionic radius, with an increase of the atomic number, which is called “lanthanide contraction” [7]. Elements Ce and Eu can also be present in oxidation states “+4” and “+2,” respectively [7, 13]. The REE are soft elements, malleable, ductile, and considered great electrical conductors, which allow their application in several industrial segments of high technology, such as automotive, nuclear, petroleum, electronic, military, metallurgical, and renewable energy [14–17]. REE can also be applied in studies of pedogenic processes, as tracers in geochemical studies [18, 19], and in agricultural fertilizers [20].

Regarding their natural distribution, the REE show regularity and follow the Oddo-Harkins rule, in which elements with an even atomic number (Ce, Nd, Sm, Gd, Dy, Er, and Yb) are more abundant than elements with an odd atomic number (La, Pr, Eu, Tb, Ho, Tm, and Lu), besides having decreasing contents with an increase in atomic mass [9]. This Oddo-Harkins rule refers to a “zigzag” standard in diagrams of composition-

Fig. 1 Graphical illustration of the sources of rare earth elements (REE) to soils (picture on the left shows the mineral apatite), where REE may undergo a series of reactions in the soil profile prior to entering the main environmental compartments



abundance, in which REE are normally presented. This standard comes from the variable concentrations that these elements have due to the inconstancy in their atomic nuclei, where the elements with even atomic numbers, by having a proton pairing in their chemical distribution, are more stable than their odd periodic neighbors [21].

In order to eliminate this zigzag standard effect and graphically demonstrate the behavior of REE in the environment, the normalization of their contents is done in the study sample, through recognized standards [22], as shown in Fig. 2. This tool helps in comprehending analytical results and allows the identification of possible abnormalities, when normalized. Several standards are used for this purpose, with the chondrite meteorites being the most used, since they are considered materials that have the same chemical composition of the material that originated the solar system bodies [24]. Besides the chondrite meteorites [23], other standards are also used such as the upper continental crust [25], the North American shale composite [26], and the Post-Archean Australian shales [27].

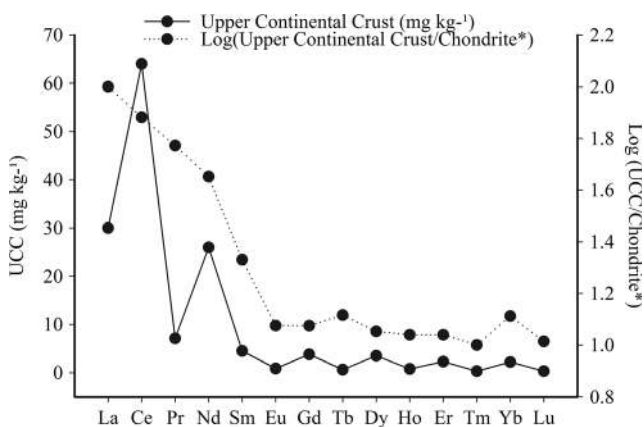


Fig. 2 Concentration (mg kg^{-1}) of rare earth elements in the upper continental crust and chondrite normalization of REE in UCC. Asterisk: data from [23]

Sources and Fate of REE in Soils

Sources

REE are found in more than 270 minerals—either primary or secondary—in a wide range of concentrations [16, 28]. Despite this, 95 % of all mineral resources containing REE in the world are concentrated in only three minerals: bastnasite, monazite, and xenotime [29].

The REE mineral content is directly proportional to its valence and ionic radius, with LREE occupying sites with the largest coordination numbers, while HREE occupy the smallest coordination numbers [30]. When a mineral has REE, it can normally contain all REE, but in different proportions and with a predominance of Ce and La [29, 31].

As many metals, the REE have affinity for oxygen and are therefore found many times in phosphatic minerals, as well as in carbonates, fluorides, and silicates [8, 32–34]. Phosphatic minerals can contain high REE concentrations, which are directly related to the mineral genesis [8, 35, 36]. However, there is a difference between LREE and HREE as regard to their enrichment in phosphatic minerals, with a predominance of a negative anomaly of Ce [37, 38]. Of the phosphatic minerals, monazite contains the highest concentration of REE, with LREE being preferentially incorporated in its structure; while in xenotime, the HREE are preferentially accommodated in its structure [39].

The availability of REE in the environment under natural conditions depends on the parent material, as well as on geochemical and biological processes [40–42]. It is known that mineral weathering is an important source of elements to the soils [43]. However, even after weathering of primary minerals, REE can still, partially or totally, be again incorporated in secondary minerals, remaining immobilized [44].

The fast increase in the exploration of mineral resources that contain REE, along with their constant application in the modern industry and everyday life, can contribute to an

increase of these elements in ecosystems [45]. The main areas with an increase of REE in the soil are restricted to regions where the agriculture is intense, to zones next to polluted sites (large cities), and/or where the parent material presents high contents of REE [46]. Industrial activities have been related with an increase of REE in soils, mainly in locations next to industrial centers [47, 48].

In agricultural areas, the main REE entrance is caused by application of phosphate fertilizers. This occurs because phosphatic rocks can present elevated concentrations of REE in their composition. Apatite is the main mineral explored for production of phosphate fertilizers, and the occurrence of REE in apatites from sedimentary and biological origin was first reported in 1878 [1]. The general formula for apatite is $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$, in which X can be fluoride, chlorine, or hydroxyl. Calcium can be substituted mainly by Na, Sr, Mn, and REE. The most common substitution is P by Si, along with a substitution of Ca by ions of trivalent REE [30].

Indirect application of REE to agricultural soils is a widespread practice, due to the use of phosphate fertilizers. However, in China, REE are deliberately applied to soils due to the enrichment of fertilizers with such elements. Since the 1980s, these fertilizers have been commonly applied in agriculture to increase seed germination, root growth, chlorophyll content, plant resistance, and agricultural productivity [20]. The amount of REE used in Chinese agriculture has been increasing year after year, reaching some thousands of tons per year. In this country, there are basically three types of fertilizers containing REE: (1) Changle (nitrates), (2) Nongle (chloride and oxides), and (3) MAR (complex with amino acids) [10, 45].

Table 1 shows REE contents reported in the worldwide literature for the main phosphate fertilizers and other products of relevant use in agriculture. It is noteworthy that phosphate products can present a great variability in their REE concentrations. Actually, due to the different sources (raw material) used for production of phosphate fertilizers, it is not uncommon to see that the same product may present different REE contents; e.g., a simple superphosphate produced in Pakistan has an average concentration of $40.2 \text{ mg Ce kg}^{-1}$, differing from the same product produced in Brazil, which had $1499 \text{ mg Ce kg}^{-1}$. This huge variation in REE content of phosphate products occurs not only due to differences in the raw material (elemental composition of the phosphate rock), but also due to variations in rock processing operations for obtaining the final product [53, 56].

A ballpark assessment of the importance of phosphate fertilizers as a source of REE for agricultural ecosystems could be used taking Brazil as an example: if we consider the apparent consumption of the main phosphate fertilizers in Brazil in 2014¹ (~4.2 million tons of monoammonium phosphate

(MAP), 5.2 million tons of single superphosphate (SSP), and 1.8 million tons of triple superphosphate (TSP)) and the concentrations reported for cerium (mg kg^{-1}) in Table 1 (449 for MAP, 1499 for SSP, and 1332 for TSP), it is estimated that the use of these fertilizers added approximately 12,000 t of Ce to Brazilian soils, only in 2014. This is not too much beyond the amounts estimated for annual consumption of important micronutrients (e.g., boron, copper, manganese, and zinc) in Brazilian agriculture.

As it was seen, the fertilizers employed in agriculture are important diffuse sources of REE for soils, even unintentionally, as it occurs in countries that are great consumers of phosphate fertilizers, such as Brazil. This might be even more relevant in the case of a deliberate enrichment of fertilizers with REE, as it occurs in China.

Soil Behavior

It is well known that the bioavailability, toxicity, and deficiency of any element in the environment depend on the element's own characteristics and the soil capacity to release it from the mineral phase or colloidal fraction. The adsorption of La, Y, Pr, and Gd depends on pH and soil cationic exchange capacity (CEC), and the availability of La, Ce, Gd, and Y increases with a decrease in pH and redox potential [58, 59].

The adsorption of REE in soils is also influenced by clay type and content, especially the concentrations of aluminum silicates and iron and manganese oxides, with these last ones having the greatest adsorption capacity [10]. Sorption of La in the surface of oxides of manganese and titanium and also in iron oxy-hydroxides varies with pH and the type of adsorbent, occurring preferably as surface precipitation, in the case of Mn oxides, and in the form of monomeric or small-molecular-weight complexes, in the surface of Ti and Fe oxides, demonstrating that mineralogy is crucial in REE behavior in soils [60, 61].

There is also a difference concerning light and heavy REE behavior in soil, with LREE being mainly associated to clayey soils, whereas HREE are more associated to sandy soils [62]. This occurs because HREE are more associated to refractory minerals (e.g., zircon), which are more resistant to weathering, and therefore remain in the coarser fraction of the soil [63].

Regarding the bond to the soil organic matter, the REE behave in a manner similar to other trace elements. Organic matter has fundamental importance in adsorption of REE, since it is a provider of negative charges to weathered soils [64]. However, it was also observed that the soluble organic fraction is responsible for REE desorption in soil, with compounds such as EDTA being able to promote the desorption of these elements, which is proportional to the concentration of acid in solution [65].

The stability of REE bonding with humic substances varies according to a molar ratio between the REE and dissolved

¹ Personal communication from ANDA, The Brazilian Fertilizer Industry Association.

Table 1 Worldwide contents of selected REE reported for major phosphate fertilizers and other particular agricultural inputs

Product	La mg kg ⁻¹	Ce	Nd	Sm	Eu	Tb	Sc	Country	Source
Single superphosphate (SSP)	18.4	40.2	–	2.0	0.4	0.3	–	Pakistan	[49]
NPK (08:23:18)	90	129	–	12	3.0	1.5	–		
Limestone	19.5	10.4	–	1.6	0.2	–	0.2	Egypt	[50]
Superphosphate	18	8.5	–	–	0.3	–	3.9		
Superphosphate	17	35	23.5	–	–	–	–	Bulgaria	[51]
NPK (12:12:17)	500	600	181	33.2	9.9	3	–	Spain	[52]
NPK (4:14:08)	534	1181	571	77	17.1	4.5	15.2	Brazil	[53]
SSP	674	1499	770	122	32.5	6.5	24.6		
Thermophosphate	755	1575	748	105	24.5	8.3	23.9		
Phosphoric acid	18.7	16.5	14.2	0.9	0.8	2.5	9.3	USA	[54]
Phosphate rock	2319	5468	1720	245	67	12	–	Brazil	[55]
Phosphogypsum	1484	3015	970	150	37	6	–		
Monoammonium phosphate (MAP)	177	449	234	43	13.6	8.7	–	Brazil	[56]
Triple superphosphate (TSP)	727	1332	556	89	29	13.7	–		
Apatite concentrate	1514	4204	1738	293	24.5	28.9	–	Iran	[14]
Fertilizer enriched with REE	15,400	24,100	1100	2000	200	25.8	–	China	[57]

organic carbon, and in these conditions, REE concentrations in solution are inversely correlated with soil pH and directly correlated with dissolved organic carbon concentrations [66, 67].

Soil Reference Concentrations

The knowledge of natural contents of an element in the soil (background concentration) is crucial for ecological and human health risk assessments. Regarding REE, this aspect deserves a special attention, because our understanding on the biological role of these elements is still in its early stages [2] and little is known about their effects in ecosystem function, which is especially relevant in areas affected by anthropogenic activities that alter natural concentrations of REE in soils.

Contents of REE naturally found in soils basically depend on the parent material, decreasing as follows: granite > basalt > sandstone [68]. Soils originated from igneous rocks, schists, and sandstone tend to contain more REE when compared to those originated from other materials [41]. Increased REE contents in areas affected by anthropogenic alterations are usually a result of the application of agricultural fertilizers [49, 52, 53, 56, 69, 70]. However, environmental factors such as rain, snow, and wind transport can contribute to these contents, mainly in areas close to large industrial sites [47].

Information is still scarce in the literature about background concentrations of REE in soils, mainly when compared with data available for many trace elements of environmental interest, such as Cd, Pb, Cr, and As. Table 2 presents reference values (natural or non-natural) for REE in soils found in several countries, as well as information regarding the method used to quantify and qualify these elements, which can be an

additional reason for a large variability found in REE reference values for soils worldwide.

Even though there are several techniques to quantify REE, the literature demonstrates that inductively coupled plasma mass spectrometry (ICP-MS) is the most used technique to determine REE in soils (Table 2). ICP-MS has a superior detection capability and presents elevated precision, currently being the most adequate technique for quantification of REE in soil extracts, either those obtained directly following an acid extraction or via a previous alkaline fusion of the materials to be analyzed [92–94].

Data from Table 2 revealed that La and Ce are the most abundant REE found in soils, with average concentrations as high as 123 and 273 mg kg⁻¹, respectively, found in soils from Uganda. These results agreed with previous reports that Ce, followed by La, is the most abundant REE in earth's crust [41]. For the sum of LREE, the highest values were found in samples from Cape Verde, followed by Bhutan. In these countries, REE contents in soils were assessed with instrumental neutron activation analysis (INAA), which could have contributed to the higher averages. The literature reports that INAA can overestimate REE values in geological samples and therefore is not the most indicated technique for REE determination, mainly for LREE [95], although INAA is used for REE determination in soil and rock samples [96]. However, these results can also be connected to the material that originated these soils.

Table 2 reveals also that samples from soils analyzed in several European countries presented very similar average values for all REE, with Denmark being an exception. The average value of the sum of REE contents (Σ REE) was higher for Croatia (216 mg kg⁻¹) and smaller for Denmark

Table 2 Contents of REE reported for soils worldwide

Country	Method*	n	Range of concentrations (average mg kg ⁻¹)									
			La	Ce	Pr	Nd	Sm	Eu	Gd	Tb		
Albania	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS	3	19–31 (25)	38–59 (52)	4.4–7.3 (5.9)	18–27 (22)	3.6–5.3 (4.5)	0.8–1.0 (0.9)	3.6–5.3 (4.3)	0.6–0.8 (0.7)		
Germany	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS, ICP-AES	79	3.7–57 (23)	7.4–115 (48)	0.8–13 (5.5)	3.2–55 (20)	0.5–8.7 (3.8)	0.1–1.6 (0.7)	0.5–7.8 (3.8)	0.1–1.1 (0.6)		
Austria	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS	18	4.0–56 (29)	8.7–106 (59)	0.9–13 (7.0)	3.5–50 (26)	0.7–10 (5.2)	0.1–2.0 (1.0)	0.8–9.5 (4.8)	0.08–1.3 (0.71)		
Australia	HCl, HNO ₃ /ICP-MS	9	2.7–24 (15)	21–120 (60)	0.8–6.8 (4.1)	2.8–24 (15)	0.4–4.6 (2.8)	0.1–1.6 (0.6)	0.6–4.3 (2.6)	0.1–0.7 (0.48)		
Belgium	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS	5	29–34 (31)	62–70 (64)	6.5–7.9 (7.3)	23–31 (28)	4.3–5.7 (5.2)	0.8–1.2 (1.0)	3.9–5.6 (5.1)	0.6–0.9 (0.8)		
Brazil	HCl, HNO ₃ , HF/ICP-MS, INAA	79	3.0–62 (20)	15–286 (82)	–	6.0–116 (25)	0.4–6.7 (3.5)	–	–	0.2–1.2 (0.7)		
Bhutan	INAA	6	41–60 (51)	82–133 (106)	–	31–44 (37)	6.4–12 (8.4)	0.9–3.2 (1.4)	–	0.8–1.2 (1.0)		
Cape Verde	INAA	63	39–413 (74)	76–685 (156)	–	44–211 (68)	7.5–25 (11)	2.2–7.5 (3.5)	–	0.8–2.1 (1.3)		
China	HNO ₃ , HF, HClO ₄ /ICP-MS, ICP-AES, INAA	852	8.0–57 (30)	18–122 (67)	1.7–12 (6.6)	6.2–41 (26)	1.2–7.8 (5.2)	0.2–2.4 (1.2)	1.6–7.1 (5.0)	0.3–1.2 (0.7)		
Croatia	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS	13	27–52 (43)	55–128 (91)	6.5–12 (10)	24–45 (39)	5.0–8.9 (7.6)	1.0–1.8 (1.5)	4.8–8.5 (7.2)	0.7–1.3 (1.0)		
Denmark	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS	5	2.6–12 (6.6)	5–23 (13)	0.5–2.7 (1.5)	2.0–10 (5.5)	0.4–1.8 (1.0)	0.1–0.4 (0.2)	0.5–1.9 (1.1)	0.1–0.3 (0.2)		
Slovakia	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS	15	6.5–41 (31)	13–84 (63)	1.5–9.6 (7.1)	5.6–36 (27)	1.0–7.0 (5.0)	0.2–1.3 (0.9)	0.9–6.6 (4.7)	0.2–1.1 (0.73)		
Spain	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS	100	5.3–128 (33)	11–246 (63)	1.3–32 (7.7)	4.6–132 (28)	0.9–23 (5.9)	0.2–7.0 (1.1)	0.9–24 (5.4)	0.1–3.7 (0.8)		
United States	HNO ₃ , HF, HClO ₄ /INAA, RNAA, ICP-MS	2	7.5–176 (33)	15–350 (67)	7.0–8.4 (7.7)	29–35 (30)	5.2–6.6 (5.9)	0.5–1.6 (1.0)	4.0–6.2 (5.1)	0.6–1.0 (0.7)		
Estonia	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS	11	5.5–37 (26)	9.6–71 (50)	1.2–9.7 (6.1)	3.5–38 (23)	0.9–8.4 (4.5)	0.2–1.6 (0.9)	0.7–9.3 (4.6)	0.1–1.3 (0.6)		
Finland	HNO ₃ , HF, HClO ₄ , Alkaline Fusion/ICP-MS, ICP-AES	319	4.8–45 (15)	8.5–90 (28)	1.0–10 (3.3)	3.4–41 (13)	0.6–6.8 (2.3)	0.3–1.3 (0.6)	0.6–6.4 (2.3)	0.07–0.9 (0.3)		
France	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS	119	2.6–66 (31)	5.5–159 (63)	0.51–4.4 (7.3)	2.1–54 (27)	0.4–11 (5.1)	0.1–2.2 (1.0)	0.4–11 (5.0)	0.05–1.5 (0.7)		
Greece	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS	41	13–64 (29)	23–102 (57)	2.9–14 (6.8)	11–53 (26)	2.1–10 (5.1)	0.5–2.4 (1.1)	2.2–11 (5.2)	0.4–1.6 (0.7)		
Netherlands	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS	8	5.6–22 (13)	12–43 (27)	1.3–5.1 (3.1)	4.7–19 (12)	0.8–3.7 (2.2)	0.2–0.8 (0.5)	0.9–3.8 (2.3)	0.1–0.5 (0.3)		
Hungary	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS	14	7.5–42 (27)	15–87 (55)	1.7–10 (6.4)	6.4–37 (24)	1.2–7.5 (4.6)	0.3–1.4 (0.9)	1.2–7.2 (4.8)	0.2–1.1 (0.7)		
Ireland	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS	11	12–36 (20)	23–78 (39)	2.5–9.1 (4.6)	9.0–35 (17)	1.4–6.6 (3.3)	0.2–1.3 (0.7)	1.4–6.4 (3.2)	0.23–1.0 (0.5)		
Italy	HNO ₃ , HF, HClO ₄ , alkaline fusion/ICP-MS	51	6.9–143 (40)	14–267 (78)	1.3–29 (8.8)	5.4–94 (32)	1.0–16 (5.9)	0.2–3.2 (1.2)	0.9–13 (5.6)	0.2–1.7 (0.8)		
Japan	HNO ₃ , HF, HClO ₄ /ICP-MS	653	0.9–120 (19)	1.1–150 (43)	0.2–31 (4.6)	0.8–120 (18)	0.2–30 (3.8)	0.04–8.1 (1.0)	0.2–27 (3.7)	0.02–3.8 (0.6)		
Latvia	HNO ₃ , HF, HClO ₄ /ICP-MS	7	11–31 (21)	21–67 (44)	2.3–8.1 (4.9)	5.5–28 (18)	1.2–5.5 (3.3)	0.3–1.1 (0.6)	1.8–5.4 (3.2)	0.2–0.9 (0.4)		

Table 2 (continued)

Country	Method*	n	Range of concentrations (average mg kg ⁻¹)												
			La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Lu	Yb	Tm	Y	
Lithuania	HNO ₃ , HF, HClO ₄ , alkaline fusion/CP-MS	16	7.9–28 (18)	15–59 (36)	1.7–7.0 (4.1)	5.9–24 (15)	1.2–5.4 (3.0)	0.2–0.9 (0.5)	1.0–4.6 (2.9)	0.2–0.7 (0.4)					
	HNO ₃ , HF, HClO ₄ , alkaline fusion/CP-MS	58	2.9–101 (21)	5.7–253 (48)	0.7–23 (5.2)	2.8–80 (20)	0.5–13 (3.7)	0.1–4.3 (0.9)	0.6–11 (3.7)	0.1–1.7 (0.5)					
Norway	HNO ₃ , HF, HClO ₄ , alkaline fusion/CP-MS	64	2.7–35 (13)	5.5–72 (27)	0.7–8.0 (3.0)	2.3–30 (12)	0.4–5.5 (2.3)	0.1–1.0 (0.3)	0.4–5.6 (1.9)	0.05–0.8 (0.3)					
	HNO ₃ , HF, HClO ₄ , alkaline fusion/CP-MS, XRF	19	19–74 (38)	38–151 (77)	4.7–18 (9.0)	16–63 (32)	2.9–10 (5.8)	0.4–2.0 (0.9)	2.8–9.3 (5.2)	0.4–1.4 (0.7)					
Portugal	HNO ₃ , HF, HClO ₄ , alkaline fusion/CP-MS	60	1.1–103 (23)	2.5–206 (48)	0.3–30 (5.6)	1.1–112 (21)	0.2–30 (4.0)	0.7–1.7 (0.8)	0.2–36 (4.1)	0.03–7.0 (0.6)					
	HNO ₃ , HF, HClO ₄ , alkaline fusion/CP-MS	10	15–35 (26)	32–80 (57)	3.3–8.6 (6.3)	13–33 (23)	2.2–6.0 (4.6)	0.4–1.2 (0.8)	2.1–5.6 (4.4)	0.3–0.9 (0.7)					
Czech Republic	HNO ₃ , HF, HClO ₄ , alkaline fusion/CP-MS	85	1.4–34 (17)	2.1–83 (37)	0.4–14 (4.2)	1.0–53 (15)	0.2–6.0 (3.0)	0.03–1.5 (0.6)	0.2–6.4 (3.0)	0.04–1.2 (0.5)					
	HNO ₃ , HF, HClO ₄ , alkaline fusion/CP-MS	10	1.7–85 (27)	3.2–117 (50)	0.4–16 (6.0)	1.5–65 (23)	0.3–13 (4.4)	0.1–2.9 (0.9)	0.2–15 (4.5)	0.04–2.1 (0.6)					
Switzerland	HNO ₃ , HF, HClO ₄ , alkaline fusion/CP-MS	9	77–134 (123)	216–291 (273)	–	51–98 (88)	–	–	–	–					
	Alkaline fusion														
Uganda															
Country	Range of concentrations (average mg kg ⁻¹)													Source	
	Dy	Ho	Er	Tm	Yb	Lu	Sc	Y							
Albania	3.8–4.8 (4.2)	0.7–0.9 (0.8)	2.1–2.8 (2.4)	0.3–0.4 (0.4)	2–2.6 (2.1)	0.2–0.4 (0.3)	10–15 (13)	–							[71]
Germany	0.5–6.0 (3.1)	0.1–1.2 (0.6)	0.3–3.5 (1.8)	0.1–0.2 (0.13)	0.1–1.5 (0.5)	0.1–0.6 (0.4)	0.8–15 (6.1)	–							[45, 71–74]
Austria	0.6–7.4 (3.9)	0.1–1.3 (0.8)	0.3–3.7 (2.2)	0.06–0.5 (0.3)	0.3–3.3 (2.1)	0.04–0.5 (0.3)	1.3–21 (12)	–							[71]
Australia	0.3–3.2 (2.1)	0.1–0.4 (0.3)	0.2–1.6 (0.8)	0.1–0.2 (0.13)	0.1–1.5 (0.5)	0.1–0.2 (0.1)	–	0.6–12 (5.3)							[75]
Belgium	3.6–5.0 (4.5)	0.7–1.2 (0.9)	2.1–3.3 (2.8)	0.3–0.5 (0.4)	2.1–3.5 (2.9)	0.3–0.6 (0.4)	7.8–14 (10)	–							[71]
Brazil	–	–	–	–	1.5–4.3 (2.9)	–	6.6–30 (18)	4.0–16 (7.8)							[47, 76, 77]
Bhutan	4.2–7.8 (5.4)	–	–	–	2.9–4.4 (3.5)	0.4–0.6 (0.5)	–	–							[62]
Cape Verde	4.5–13 (7.1)	–	–	–	–	0.1–0.9 (0.3)	6.0–44 (25)	–							[78]
China	2.0–6.3 (3.9)	0.3–1.2 (0.8)	0.8–3.1 (2.2)	0.1–0.4 (0.2)	0.6–2.7 (2.1)	0.1–0.4 (0.3)	11–13 (12)	14–35 (27)							[46, 79–82]
Croatia	3.8–7.0 (6.0)	0.8–1.4 (1.2)	2.3–4.2 (3.6)	0.3–0.6 (0.5)	2.1–4.0 (3.5)	0.3–0.6 (0.5)	7.7–16 (13)	–							[71]
Denmark	0.5–2.2 (1.1)	0.1–0.4 (0.2)	0.3–1.3 (0.7)	0.05–0.2 (0.1)	0.4–1.5 (0.9)	0.05–0.2 (0.1)	0.9–3.9 (2.2)	–							[71]
Slovakia	1.1–5.9 (4.2)	0.2–1.2 (0.9)	0.7–3.4 (2.5)	0.1–0.5 (0.3)	0.8–3.3 (2.4)	0.1–0.5 (0.4)	2.0–15 (10)	–							[71]
Spain	0.7–23 (4.4)	0.1–4.8 (0.9)	0.3–14 (2.5)	0.04–2.1 (0.3)	0.4–13 (2.3)	0.03–2.0 (0.3)	1.3–54 (10)	–							[71]
United States	–	0.9–1.5 (1.2)	1.5–2.2 (1.9)	0.3–0.6 (0.4)	2.3–3.5 (2.9)	0.3–0.5 (0.4)	2.8–17 (9.9)	3.8–169 (16)							[83]

Table 2 (continued)

Country	Range of concentrations (average mg kg ⁻¹)											Source
	Dy	Ho	Er	Tm	Yb	Lu	Sc	Y	Y	Y	Y	
Estonia	0.7–7.2 (4.0)	0.2–1.3 (0.8)	0.5–3.8 (2.2)	0.07–0.5 (0.3)	0.6–3.2 (2.1)	0.1–0.5 (0.3)	1.3–10 (6.4)	–	–	–	–	[71]
Finland	0.5–4.8 (2.0)	0.1–1.1 (0.4)	0.3–3.2 (1.2)	0.05–0.5 (0.1)	0.4–3.4 (1.2)	0.04–0.5 (0.1)	2.0–21 (8.1)	–	–	–	–	[71]
France	0.3–8.6 (4.2)	0.04–1.8 (0.8)	0.2–5.0 (2.4)	0.02–0.71 (0.3)	0.2–4.5 (2.3)	0.01–0.7 (0.3)	0.3–29 (9.3)	–	–	–	–	[71]
Greece	2.1–9.2 (4.5)	0.4–1.9 (0.9)	1.2–5.3 (2.5)	0.2–0.7 (0.3)	0.8–5.0 (2.4)	0.1–0.7 (0.3)	4.4–23 (14)	–	–	–	–	[71]
Netherlands	0.6–3.0 (1.9)	0.1–0.6 (0.4)	0.4–1.8 (1.1)	0.09–0.3 (0.2)	0.3–1.9 (1.1)	0.08–0.3 (0.1)	0.9–9.5 (4.3)	–	–	–	–	[71]
Hungary	1.1–5.8 (3.9)	0.2–1.2 (0.8)	0.8–3.7 (2.4)	0.1–0.5 (0.3)	0.8–3.4 (2.3)	0.1–0.5 (0.3)	2.9–17 (9.0)	–	–	–	–	[71]
Ireland	1.3–5.8 (3.1)	0.3–1.2 (0.6)	0.8–3.1 (1.8)	0.1–0.5 (0.2)	0.9–3.0 (1.7)	0.2–0.4 (0.3)	3.2–12 (6.5)	–	–	–	–	[71]
Italy	0.9–8.9 (4.5)	0.2–1.7 (0.9)	0.6–4.9 (2.5)	0.1–0.7 (0.3)	0.7–4.1 (2.3)	0.1–0.6 (0.3)	5.5–21 (11)	–	–	–	–	[71]
Japan	0.1–25 (3.4)	0.02–4.3 (0.7)	0.1–13 (2.0)	0.01–1.5 (0.2)	0.06–12 (1.9)	0.01–1.5 (0.2)	0.4–56 (17)	–	–	–	–	[84–86]
Latvia	1.4–5.1 (2.9)	0.3–1.0 (0.6)	0.9–2.7 (1.6)	0.1–0.4 (0.3)	0.9–2.9 (1.8)	0.2–0.4 (0.3)	1.8–11 (5.8)	–	–	–	–	[71]
Lithuania	1.1–4.6 (2.6)	0.2–0.8 (0.5)	0.8–2.2 (1.5)	0.1–0.4 (0.2)	0.8–2.6 (1.6)	0.1–0.3 (0.2)	1.8–7.6 (4.3)	–	–	–	–	[71]
Norway	0.8–9.0 (3.4)	0.9–1.8 (0.7)	0.6–5.0 (2.1)	0.09–0.8 (0.3)	0.6–5.8 (2.2)	0.1–0.8 (0.3)	2.5–33 (11)	–	–	–	–	[71]
Poland	0.4–5.1 (1.8)	0.1–1.0 (0.4)	0.3–3.1 (1.2)	0.05–0.5 (0.1)	0.3–3.4 (1.2)	0.05–0.5 (0.2)	0.7–12 (3.4)	–	–	–	–	[71, 87]
Portugal	1.8–7.1 (3.7)	0.3–1.3 (0.7)	0.9–3.6 (2.0)	0.1–0.6 (0.3)	0.7–3.5 (1.9)	0.1–0.5 (0.2)	1.9–20 (8.7)	–	–	–	–	[71]
UK	0.2–45 (3.8)	0.03–9.2 (0.8)	0.1–26 (2.3)	0.01–4.0 (0.3)	0.09–25 (2.3)	0.02–3.2 (0.3)	0.7–23 (9.4)	–	–	–	–	[71]
Czech Republic	1.9–5.1 (4.1)	0.4–1.0 (0.8)	1.1–3.3 (2.5)	0.2–0.5 (0.3)	1.2–3.2 (2.5)	0.2–0.5 (0.3)	3.6–28 (11)	–	–	–	–	[71]
Sweden	0.9–6.2 (2.9)	0.03–1.3 (0.6)	0.1–4.0 (1.8)	0.09–0.6 (0.2)	0.07–4.2 (1.9)	0.09–0.6 (0.3)	0.9–16 (7.6)	–	–	–	–	[71, 74, 88–90]
Switzerland	0.2–13 (3.8)	0.1–2.7 (0.8)	0.1–7.9 (2.2)	0.02–1.1 (0.3)	0.1–7.1 (2.0)	0.02–1.0 (0.3)	0.7–15 (8.8)	–	–	–	–	[71]
Uganda	–	–	–	–	–	–	–	–	–	–	–	[91]

Range of concentrations and average values—inside parenthesis—obtained via different analytical methods

n number of observations

* Sample preparation/sample analysis

(32 mg kg⁻¹). Since phosphate fertilizers are one of the main diffuse sources of REE to soils [46, 97, 98], we could expect higher average Σ REE for soils of France, Spain, and the UK, which are historically the major consumers of phosphate fertilizers in Europe (P₂O₅ consumption taken from IFA database – www.fertilizer.org/statistics). However, this was not observed. Data from Table 2 suggests that the sources and the behavior of REE in European soils tend to be very similar.

In order to evaluate a potential influence of the addition of phosphate fertilizers over the content of REE in European soils, the data collected for European countries (Table 2), as well as the contents of REE from Upper Continental Crust and from an apatite of sedimentary origin (main raw material used in the production of phosphate fertilizers marketed in Europe), were normalized to a standard material, i.e., the average REE concentrations found in chondrites, as proposed by [23] (Fig. 3).

The REE signatures for European soils are very similar to that of the Upper Continental Crust (UCC), which, by its turn, differs from the typical signature of an apatite of sedimentary origin derived from Morocco, a large exporter of phosphate fertilizers to Europe. The fact that the typical signature of the Morocco apatite is distinct from those observed for European soils (Fig. 2) indicates that even though phosphate fertilizers are considered the main diffuse source of REE to the environment, its intense and continuous application in Europe was not enough to alter the typical signature of these elements in the soils. Actually, Fig. 2 reveals not only that the current status of REE in European soils was not affected by intense anthropogenic activity caused by continuous additions of REE from phosphate fertilizers, but also indicates that REE

concentrations in European soils are compatible with the global average.

Finally, with respect to yttrium (Y), even though this element is recognized as a REE, there is little information in the literature regarding reference concentrations of this element in soils. Values for Y in soil were found only in studies done in seven countries, with averages varying from 5.3 mg kg⁻¹, in Australia, to 27 mg kg⁻¹, in China.

REE in Plants

Since the 1970s, there are reports of commercial application of REE in Chinese agriculture, with indication of yield increases in several crops [100, 101].

Many hypotheses have been currently proposed for REE effects on plant growth and development, not only at the metabolic level, but also at the structural and cytogenetic levels [102–104]. Hypotheses supporting the beneficial effects of REE in plant metabolism include stimulation of the antioxidant system, increased nutrient absorption, increased nitrogen and CO₂ fixation, and positive effects on biomass production by induction of a higher photosynthetic rate, due to an increase in electron transport rate in the photochemical phase of photosynthesis [105]. Regarding the plant structural level, the hypotheses vary from the substitution of Ca in cell wall structure, in cytoskeleton, and in membranes and cytoplasmic organelles [106, 107], to modifications in size and density of anatomic structures such as stomata, trichomes, and tissue thickness [103]. At the cytogenetic level, the REE-associated benefits are linked to an increase in the mitotic index [102,

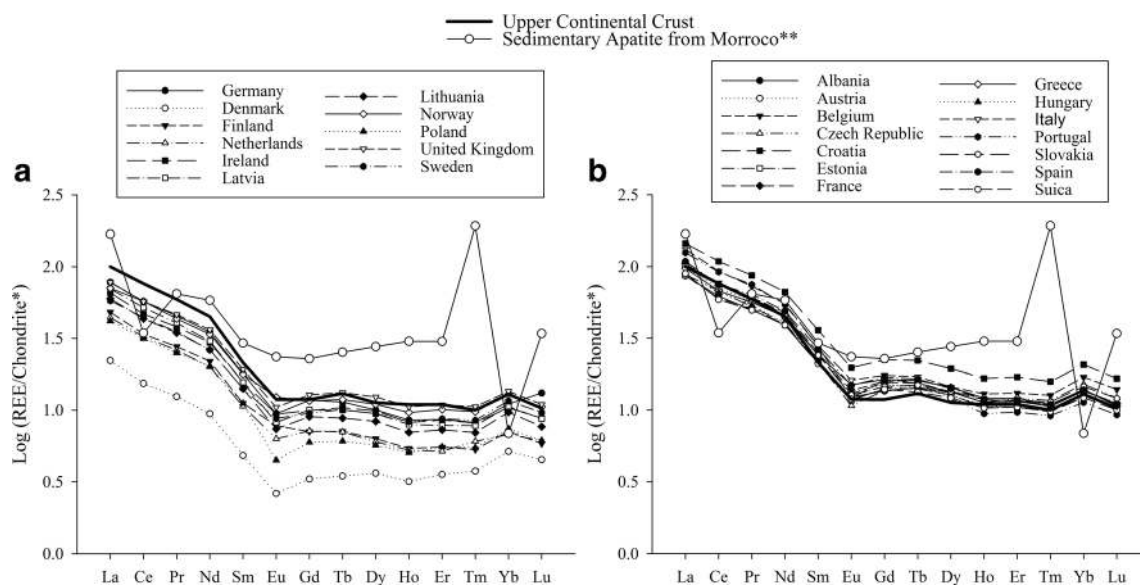


Fig. 3 Chondrite normalized REE distribution patterns of UCC compared with a sedimentary apatite from Morocco and with average values of soils from different European countries. Countries on the left

(a) show a trend of REE depletion in soils relative to UCC, whereas countries on the right (b) show a trend of REE enrichment relative to UCC. *Single asterisk*: data from [23]; *double asterisk*: data from [99]

104], as well as to the development of abnormalities in the cell cycle that benefit the production of biomass, such as the appearance of binucleated cells [102]. Some REE action mechanisms in plants, as well as effects found in recent studies, are reported in the following topics, with data compiled in Table 3.

REE Uptake, Distribution, and Contents in Plants

REE concentrations in plants vary according to the contents of these elements in the environment and among different plant species [121]. Due to their higher mobility in soils, LREE are more easily absorbed by plants, thus occurring at greater contents than HREE in plant tissues. In fact, citrus plants have recently been described as REE bioaccumulators, accumulating especially LREE [144]. In addition, since HREE form much more stable complexes in soil solution, preferential absorption of LREE is favored [145].

Other factors affecting REE uptake in soil solution are the levels of nitrogen, potassium, and phosphate fertilization. REE absorption is facilitated following an increase in the rates of nitrogen and potassium fertilization, while phosphate fertilization renders the absorption of these elements more difficult [146].

Plants have a range of features that affect REE redistribution, especially those related to the presence of apoplastic barriers. Initially, the apoplastic barriers situated in the roots are the first obstacles for these elements to reach the xylem, thus impairing their translocation to remaining plant organs. Due to this fact, the contents of REE found in different plant organs follow the sequence: roots > stems > leaves > flowers > fruit > seeds [140, 145].

REE absorption occurs also thru foliar applications. Under these circumstances, the apoplastic barriers continue to work as obstacles to the translocation of these elements to different plant parts. However, in this case, the distribution of these elements follows the order: leaves > stems > roots > flowers > fruit > seeds [145].

Within the saps of the xylem or phloem, where REE are translocated/remobilized, the redistribution is generally regulated by mechanisms that control the nutrient flow, i.e., the transpiratory rate, in the case of the xylem, and the source-drain system (osmosis control), in the case of the phloem. Inside the vascular tissues, the REE can bind reversibly to anions such as COOH^- , with the degree of bonding varying according to the atomic number of the element of interest [97], which may also influence the accumulation of these elements [97, 147]. Inside the plants, most REE are bonded to cell walls [106, 148]. However, some REE can cross the cell membrane, accumulating in organelles as crystals such as “REE oxalates” [102, 107] or even in root cortical tissues, which also avoids translocation to plant shoots.

As seen, the effects of REE on plants can be either direct, due to their presence in plant structures, or indirect—mainly in the shoot—for triggering processes through secondary messengers that cause a cascade effect on metabolic processes. Owing to this fact, plant processes affected by the presence of REE are quite complex and still need to be better elucidated. Some effects of REE on plant metabolism, development, and anatomy are described in the next sections, with detailed information provided in Table 3.

Effects of REE on Plant Metabolism

Water Use Efficiency

It has been reported that REE have a positive effect on water use efficiency by plants due to an increase in the content of proline, an amino acid with a high ability for hydration, which makes the plant more resistant to water stresses [108, 110, 111]. There are also studies reporting the advantages of increased proline content in the presence of REE, eliminating reactive oxygen species (ROS) and promoting the inhibition of lipid peroxidation [109, 112].

Photosynthesis (Photochemical Phase)

Since REE have the chemical property of electric conductors, being therefore used in several industry sectors, there is a hypothesis that this chemical property can also leverage electronic flow processes in plant species [105]. The performance of REE as electron conductors in plants could be associated with the photosynthesis Z scheme, i.e., with the photochemical phase of photosynthesis. In this manner, REE can increase the electronic flow in the photochemical phase, decreasing energy dissipation to other processes besides the photosynthetic. REE can also increase the potential quantum yield of photosystem II, allowing that the larger electronic flow, caused by REE, be used for production of a greater amount of energy and reducing power, favoring the whole photosynthetic process, and consequently the biomass production in plants [105, 113–115].

Photosynthesis (Biochemical Phase)

The energy increase and the reducing power generated by the photochemical phase of photosynthesis, in the presence of REE, favor also the biochemical phase of photosynthesis. However, besides this stimulus from a higher reducing power and increased energy available for Calvin cycle reactions, the REE can leverage gas exchanges, especially the stomatal conductance, which increases the photosynthetic rate, due to a higher CO_2 assimilation for the photosynthetic process [102, 118]. It is also broadly reported that besides favoring the photosynthesis through increasing gas exchanges, REE increase

Table 3 REE's effects in plant physiology

Element	Concentration	Media	Species	Effect	Source
Water use efficiency					
Ce	89.26–446.03 μM	Soil-vessel	<i>Vigna unguiculata</i>	Increase the proline content.	[108]
	10, 30, 50, and 100 μM	Nutrient solution	<i>Hydrilla verticillata</i>	No change in the content of proline up to 10 μM of Ce; starting at 30 μM : progressive increase of proline content.	[109]
La	10 μM	Nutrient solution	<i>Hypericum perforatum</i>	Increase the proline content.	[110]
	40, 80, 120, and 160 μM	Nutrient solution	<i>Hydrocharis dubia</i>	Induction of proline accumulation, according with the increase of La content; the highest level of proline was observed at 160 μM , which was increased by 293 %, compared to the absence of La.	[111]
Y	10, 30, 50, and 100 μM	Nutrient solution	<i>Hydrilla verticillata</i>	No change the proline content up to 10 μM of La; starting at 30 μM : progressive increase in the content of proline according with the La applied.	[109]
	30, 150, 300, 600, and 900 mg kg^{-1}	Soil-vessel	<i>Oryza sativa</i>	Increase the proline content.	[112]
	10^{-5} , 10^{-4} , and 10^{-3} mol L^{-1}	Nutrient solution	<i>Zea mays</i>	Decreased of the free proline concentration in roots and shoots, more pronounced in leaves; decrease of water content (starting at 10^{-3} mol L^{-1}) and the water use efficiency (starting at 10^{-4} mol L^{-1}), respectively.	[103]
Photosynthesis					
Photochemistry phase					
Ce	10 μM	Foliar application	<i>Oryza sativa</i>	Increase in the quantum yield (Fv/Fm) of the photochemical stage.	[113]
	n.d.*	Isolated chloroplasts	<i>Spinacia oleracea</i>	Increase the yield of chlorophyll fluorescence and electron transport rate.	[105]
Y	20 μM	Nutrient solution	<i>Zea mays</i>	Under magnesium deficiency conditions: prevented the inhibition of the synthesis of photosynthetic pigments (chlorophyll and carotenoids), improved light absorption and transformation of energy, evolution of oxygen, and photophosphorylation activity and its coupling factor Ca^{2+} -ATPase.	[114]
	10^{-5} , 10^{-4} , and 10^{-3} mol L^{-1}	Nutrient solution	<i>Zea mays</i>	Decrease the gas exchange (photosynthetic rate, transpiration rate, and stomatal conductance) and the content of photosynthetic pigments (chlorophyll <i>a</i> and <i>b</i> and carotenoids), adversely affecting the photosynthetic process.	[103]
Light REE					
Ce	n.d.*	Mining soil (isolated chloroplasts)	<i>Dicranopteris dichotoma</i>	Increase the efficiency of PSII and electron transport rate.	[115]
	mg kg^{-1}	Mining soil (isolated chloroplasts)	<i>Dicranopteris dichotoma</i>	Increase the efficiency of PSII and electron transport rate.	[116]
	La—55.27				
	Ce—160.53				
	Pr—12.26				
	Nd—47.56				
Sm—10.13					
Eu—2.43					
Gd—11.67					
Biochemistry phase					
Ce	0.5 $\mu\text{mol L}^{-1}$	Tissue culture	<i>Arabidopsis thaliana</i>	Increase the chlorophyll content.	[117]
La	81.6 μM	Nutrient solution	<i>Oryza sativa</i>	Increase the photosynthetic rate and stomatal conductance.	[118]

Table 3 (continued)

Element	Concentration	Media	Species	Effect	Source
Y	5 and 10 μM	Nutrient solution	<i>Glycine max</i>	Stimulation the photosynthetic rate and the total chlorophyll content.	[102]
Physiological role of calcium in plants	10^{-5} , 10^{-4} , and 10^{-3} mol L^{-1}	Nutrient solution	<i>Zea mays</i>	Decrease the stomata size and increase the stomatal density on both sides of adaxial and abaxial epidermis.	[103]
	4, 20, 40, 120, 200, and 400 μM	Foliar application	<i>Amoracia rusticana</i>	Increase production of H_2O_2 that causes a stimulus to the increase influx of extracellular Ca^{2+} and Ca^{2+} release structure; causing the overload of Ca^{2+} and inhibition of biochemical processes controlled by this element as a second messenger.	[119]
La	5, 10, 20, 40, 80, and 160 μM	Nutrient solution	<i>Glycine max</i>	Disruption the cell walls by Ca replacement by La, according with the increase the La content.	[102]
Gd	1.0 mmol L^{-1}	Tissue culture	<i>Oryza sativa</i>	Appearance of irregularities in the cell wall structure due to the replacement of Ca by La.	[106]
	100, 200, 300, 400, and 500 $\mu\text{mol L}^{-1}$	Isolation of mitochondria (nutrient solution)	<i>Oryza sativa</i>	Inhibition of Ca channels.	[120]
Mineral nutrition					
Ce	n.d.*	Soil-vessel	<i>Amoracia rusticana</i>	Ce penetrates by the apoplast and symplast way.	[121]
La	5, 10, 20, 40, 80, and 160 μM	Nutrient solution	<i>Glycine max</i>	Increase the content of Ca, P, K, and Mn, while Cu and Fe levels decreased.	[102]
Eu	0.08, 0.24, and 1.20 mmol L^{-1}	Nutrient solution	<i>Glycine max</i>	Increase the ion uptake.	[122]
	0.05 to 1.5 mg L^{-1}	Soil-vessel	<i>Oryza sativa</i>	Higher growth and nutrient absorption.	[123]
Y	0.01 mg L^{-1}	Soil-vessel	<i>Triticum aestivum</i>	Improve uptake and distribution of nutrients.	[124]
	1, 2, 4, and 5 mg L^{-1}	Nutrient solution	<i>Nymphoides peltata</i>	Nutritional imbalance.	[125]
Ce and La	0.2, 1.0, and 5.0 mM La or Ce	Nutrient solution	<i>Zea mays</i> and <i>Vigna unguiculata</i>	Negatively affects mineral nutrition.	[126]
All ETR	mg g^{-1} La—12.46 Ce—26.96 Pr—5.20 Nd—7.80 mg kg^{-1} Sm—544.41 Eu—83.04 Gd—91.92 Tb—40.85 Dy—8.92 Ho—3.90 Tm—8.76 Yb—7.79 Lu—3.28 Y—140.05 $\mu\text{g g}^{-1}$ La—35.7 Ce—79.2 Pr—8.92 Nd—34.7 Sm—6.85 Eu—1.39 Gd—5.73 Tb—0.876	Mining soil	<i>Zea mays</i> and <i>Sorghum bicolor</i>	Increase the growth and nutrient absorption.	[127]
All ETR		Soil	<i>Helianthus annuus</i>	Increase absorption of other elements with no known biological function, such as Cd.	[128]

Table 3 (continued)

Element	Concentration	Media	Species	Effect	Source
Enzymes					
Ce	Dy—5.12 Ho—1.01 Er—2.859 Tm—0.409 Yb—2.70 Lu—0.409	Tissue culture	<i>Tetrasigma hemsleyanum</i>	Increase the flavonoid production by higher enzyme activity.	[129]
	100 μM	Nutrient solution	<i>Oryza sativa</i>	Ameliorating the Cd toxicity by increasing activity of enzymes of the antioxidant system and decrease the oxidative stress.	[113]
La	<120 $\mu\text{mol L}^{-1}$	Nutrient solution	<i>Vicia faba</i>	Increase the activity of superoxide dismutase, catalase, guaiacol peroxidase and ascorbate peroxidase, and the heat shock protein 70 (HSP 70).	[130]
	40, 80, 120, and 160 μM	Nutrient solution	<i>Hydrocharis dubia</i>	Induction of antioxidant system.	[111]
	0.08, 0.24, and 1.20 mmol L^{-1}	Nutrient solution	<i>Glycine max</i>	Mitigation of the deleterious effects of UV-B radiation, the greater activation of antioxidant system.	[122]
Tb	20, 80, 320, and 1280 μM	Soil-vessel	<i>Amoracia rusticana</i>	Increase the peroxidase activity and content of lignin.	[119, 131]
La and Ce	100 mg L^{-1}	Foliar application	<i>Brassica chinensis</i>	Increase the soluble sugar content and vitamin C for most enzymatic action.	[132]
Plant development					
Germination					
Ce	5, 10, 15, 20, and 25 mg L^{-1}	Soil	<i>Zea mays</i>	Promotes improvements in seed quality.	[133]
Eu	0.01 mg L^{-1}	Soil-vessel	<i>Triticum aestivum</i>	Increase the germination.	[124]
Growth					
Ce	100 μM	Tissue culture	<i>Tetrasigma hemsleyanum</i>	Increase the biomass growth.	[129]
	5, 10, 15, 20, and 25 mg L^{-1}	Soil	<i>Zea mays</i>	Increase the crop yield.	[133]
La	0.05 to 1.5 mg L^{-1}	Soil-vessel	<i>Oryza sativa</i>	Increase the growth.	[123]
Eu	0.01 mg L^{-1}	Soil-vessel	<i>Triticum aestivum</i>	Increase the growth of roots and leaves with better architecture and structure.	[124]
La and Ce	100 mg L^{-1}	Foliar application	<i>Brassica chinensis</i>	Promotion of shoots higher, growth of most fresh and dry weight of leaves and stems, and the higher proportion of dry weight/wet weight. (More on Ce treatments than La).	[132]
Eu and Ce	10 and 50 mg L^{-1} , of Eu and Ce, respectively	Soil	<i>Triticum aestivum</i> and <i>Secale cereale</i>	Increase the biomass yield.	[134]
All REE	La—12.46 Ce—26.96 Pr—5.20 Nd—7.80 mg kg^{-1} Sm—544.41 Eu—83.04 Gd—91.92 Tb—40.85 Dy—8.92 Ho—3.90	Soil	<i>Zea mays</i> and <i>Sorghum bicolor</i>	Increase the growth.	[127]

Table 3 (continued)

Element	Concentration	Media	Species	Effect	Source
Phytohormones	Tm—8.76 Yb—7.79 Lu—3.28 Y—140.05				
	10 $\mu\text{mol L}^{-1}$	Tissue culture	<i>Arabidopsis thaliana</i>	Inhibition the content and action of the abscisic acid.	[135]
	4, 20, 40, 120, 200, and 400 μM	Foliar application	<i>Amoracia rusticana</i>	Reduction the content of gibberellin and auxin and increase the abscisic acid levels.	[119]
	5 $\mu\text{mol L}^{-1}$	Tissue culture	<i>Dendrobium densiflorum</i>	Maintenance the total levels of endogenous cytokinin and increase the endogenous and auxin.	[136]
Internal structural changes Chromosomes-cell cycle					
	5, 10, 20, 40, 80, and 160 μM	Nutrient solution	<i>Glycine max</i>	Increase the mitotic index; Appearance of binucleate cells (starting at 5 μM); Appearance of c-metaphase (starting at 10 μM); Greater induction of c-metaphase (starting at 20 μM). Affects the stabilization of the cytoskeleton.	[102]
	1, 10, 100, and 1000 μM and 10 mM 0.1, 1, and 10 mM of REE solution (La 100.07; Ce 327.57; Pr 25.76; Nd 0.14, and Gd 0.006 mM)	Tissue culture Nutrient solution for seed germination test	<i>Zea mays</i> <i>Triticum durum</i>	Decrease in mitotic index according to the REE concentration	[137] [104]
Organelles					
	50, 100, 200, and 400 μM	Isolation of mitochondria (nutrient solution)	<i>Oryza sativa</i>	Increase the membrane permeability.	[138]
Ce	5, 10, 20, 40, 80, and 160 μM	Nutrient solution	<i>Glycine max</i>	Loss of the original shape (ellipsoidal shape) of chloroplasts and thylakoids, which presented a disorganized arrangement; Loss of the globular configuration of mitochondria and fewer mitochondrial cristae and intermembrane space greater; Damages in nuclear membrane were also observed. La accumulation was not verified in the same places that the Ca, but mainly in the chloroplasts.	[102]
	1 mmol L^{-1}	Tissue culture	<i>Dryopteris erythrosora</i>	Loss of the original format of organelles.	[139]
La	1 mmol L^{-1}	Tissue culture	<i>Oryza sativa</i>	Increase the root membrane permeability.	[106]
	0.08, 0.24, and 1.20 mmol L^{-1}	Nutrient solution	<i>Glycine max</i>	Mobile gradient Y was as follows: cell wall > organelle > soluble fraction.	[122]
Y	1, 2, 4, and 5 mg L^{-1}	Nutrient solution	<i>Nymphaoides peltata</i>	Increase the membrane permeability.	[125]
Eu	500 $\mu\text{mol L}^{-1}$	Tissue culture	<i>Oryza sativa</i>	Increase the mitochondria's size, causing the collapse of the membrane, mitochondrial fluidity, and decrease in membrane permeability, besides the modification of the ultrastructure of mitochondria.	[140]
	20, 60, 100, 200, 300, 400, and 500 $\mu\text{mol L}^{-1}$	Tissue culture	<i>Oryza sativa</i>	Mitochondrial biogenesis was negatively affected by disorders in mitochondrial permeability.	[120]
Gd	20 and 200 μM	Foliar application	<i>Amoracia rusticana</i>	Worsening of oxidation of unsaturated fatty acids; Decreased membrane fluidity; occurrence of damage to the plasma membrane and loss the membrane proteins function ; Decrease the exchange for extracellular/intracellular substance, leading to changes in intracellular nutrient content.	[141]

Table 3 (continued)

Element	Concentration	Media	Species	Effect	Source
La and Ce	30, 200, and 500 mg kg ⁻¹	Soil-vessel	Guanglin 9 (<i>Eucalyptus grandis</i> × <i>Eucalyptus urophylla</i>) and <i>Eucalyptus grandis</i> 5	Disruption the cell wall and membranes.	[142]
Tissues					
La	10 and 40 μM	Nutrient solution	<i>Pistia stratiotes</i>	Induction of coif growth of the coif.	[143]
Y	10 ⁻⁵ , 10 ⁻⁴ , and 10 ⁻³ mol L ⁻¹	Nutrient solution	<i>Zea mays</i>	Decrease the stomata size and increased stomatal density on both sides of the adaxial and abaxial epidermis.	[103]

the content of photosynthetic pigments such as chlorophyll, which contributes for a higher photosynthetic rate [102, 114, 117].

Calcium-Like Physiological Effects

The REE, La in special, can act as Ca replacements, mainly in plant structure, bonding with cell walls in which Ca would be part of the composition and replacing it in its function as a secondary messenger [106].

Due to the fact that La and Ca are chemically and physically similar, the manner that they act is similar in plants, inducing the competition and substitution of Ca by La [20, 149]. This replacement in general promotes structural modifications [106, 120], such as loss of structuring in the medium lamella. La can also replace Ca in the protoplasm, chloroplasts, mitochondria, and cytoplasmic membranes [102, 107]. Besides this, La can replace Ca in Ca oxalate crystals, which are present in many plant tissues [103]. Similarly to La, other REE have also been associated to this type of Ca replacement, due to their very similar ionic radius [118, 120].

Mineral Plant Nutrition

The effects of REE in plant mineral nutrition are varied. Some studies report synergism with some elements, while others show antagonism [124, 126, 127, 149, 150]. For some species, the presence of REE can promote beneficial effects on uptake and translocation of nutrients such as nitrogen, thus increasing the production of amino acids and proteins, which will act in several metabolic routes, leveraging plant vital processes [97].

Other nutrients such as Fe, Cu, and Mn can also have their absorption increased in the presence of REE, in several species. This can increase the amount of cofactors involved in several metabolic processes and promote an increase in plant growth [102, 127, 134, 150]. In addition, there are reports that the presence of REE may lead also to an increased absorption of other elements with no known biological function, such as Cd [128].

Enzymatic System

The stimulus to enzyme production and activation in plants, due to the presence of REE, is associated with an influx of nutrients that constitute these enzymatic molecules and also to a higher influx of cofactors and catalysts of enzymatic reactions that will trigger their activity [129, 132]. There are also studies that correlate the presence of REE to a higher activity of the antioxidant enzymatic system [112, 117, 119, 130, 131, 150].

Effects of REE on Plant Development

Seed Germination

Some studies report positive effects of REE in seed germination, mainly because these elements act in a synergistic manner with phytohormones that stimulate germination, besides inhibiting phytohormones that negatively affect seed germination, as it will be described further [124, 133].

Plant Growth

It has been broadly reported that REE positively influence plant growth, increasing biomass production [127, 129, 132, 134, 149]. Other factors related to plant growth that contribute to an increase of productivity, such as better plant structuring and architecture, have been also associated with the presence of REE [124].

Phytohormones

The production of phytohormones is affected by the presence of REE, and this interaction has been proposed as one of the mechanisms through which these elements can influence plant growth. However, it is not clear yet if REE are directly involved with signalization of plant hormones, and the responses regarding stimulus or inhibition of phytohormones are variable among species and among REE [119]. While a synergism has been reported between the presence of Tb and the production and action of abscisic acid, the opposite was observed regarding auxin and gibberellin [119]. On the other hand, Nd did not influence total levels of endogenous cytokinin and significantly increased the level of auxin [136].

Effects of REE on Plant Internal Structure

Chromosomes-Cell Cycle

It is reported that REE may act as inducers of the cell cycle, increasing or reducing the mitotic index in plants [102, 104]. Besides altering the mitotic index, at low concentration, La was described to promote the appearance of abnormalities in the cell cycle, favoring biomass growth due to the duplication of the cell genome; i.e., the appearance of polyploidized cells (binucleated) resulted in increasing tissue size. Yet, a further increase in La concentration led to the appearance of abnormalities such as c-metaphases, indicating La toxicity [102]. Moreover, there are studies demonstrating that REE may cause destabilization of the cytoskeleton, affecting the cell cycle [137].

Organelles

Since REE can bind to plant structures, they can cause cell destructuring (by Ca replacement). These destructuring processes are commonly verified in cell walls [125, 142] and also occur frequently in chloroplasts, mitochondria, and nuclei that lose their original format [102, 106, 140]. The main reports of REE effects on membrane stability are associated to alterations of stability, functionality, and permeability [120, 138, 140, 150, 151].

Tissues

There are reports that root protecting tissues (cap), which have direct contact with REE present in soil solution, can be increased, as a protection to their excessive influx, which constitutes the mechanism of plant tolerance to these elements. Besides this, other tissues can be thickened, such as apoplastic barriers, to avoid the translocation of these elements to shoots [143]. Additionally, the dimensions and density of structures such as the stomata can be modified as a way to keep the photosynthetic process in the presence of these elements [103].

Ecological and Human Health Risks Associated with REE

Even though many medical and pharmacological studies have been reported with REE [152–156], so far, little attention has been given to ecological and environmental aspects related to the presence of REE in soils and their possible transference in the trophic chain [157, 158].

Several studies involving effects of REE in experimental animals have reported an accumulation of these elements with time. The main spots for accumulation are the bones, liver, and lungs [156, 159, 160]. Some damage can be mentioned, such as cardiac, hepatic, hematological, and renal problems, besides effects in the gastrointestinal tract, in bones, in the central nervous system, and in the pulmonary and cytogenetic systems [79, 156, 159–162]. Despite this, the current information is not enough to determine the safe levels of exposure in humans [160], with values found being described as temporary [163].

In studies that evaluate the risk to human health, the dose representing an estimate, with uncertainty spanning perhaps an order of magnitude, of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime is called oral reference dose (RfD) [160, 161]. Toxicological studies provide a basis for deriving non-observed adverse effect level (NOAEL) and lowest observed adverse effect level (LOAEL) contents. By applying

uncertainty and modification factors (specific to each condition), values for RfD are obtained [160, 161]. It is possible to compare the toxicity of different substances through RfD values. These values are used to estimate the risk for a certain group, by comparing the exposure level to the effect level (RfD). Table 4 presents RfD values for some REE. The existence of a distinct toxicity between the elements and for one element alone is emphasized in this table, depending on its accompanying ion.

Even though these data are useful to evaluate potential risks of REE to humans, only in specific cases, there will be direct exposure to salts/oxides of these elements. In most cases, the major exposure routes will be ingestion of food, water, and contaminated soil, as well as dermal contact and inhalation of fumes and particulate materials [163]. Therefore, it is necessary to know the real doses to which the organisms are exposed to.

There are evidences that REE may accumulate in the soil surface due to their sorption onto soil colloids [79, 157], which consequently can lead to low bioavailability. This is directly affected by factors such as pH and the presence of organic and inorganic ligands [158]. Under these circumstances, if there is ingestion of REE-contaminated soil, the total content of the element possibly would not represent the real risk.

For better risk estimates of soil-derived REE, it would be necessary to perform bioaccessibility studies, such as those implemented by Smith et al. [91], who evaluated bioaccessible contents (physiologically based extraction test) of La, Ce, and Nd in soil samples (ground soils) and soils eaten deliberately, such as termite nest soils and traditional herbal-soil remedies, in the district of Mukono (Uganda). The average bioaccessibility varied from 2.9 to 14 % for La, 1 to 15 % for Ce,

and 3.4 to 19 % for Nd. A smaller bioaccessibility was observed in soil samples, when compared with the other materials evaluated. The authors concluded that the low bioaccessible levels of Ce considerably reduce the contribution of Ce exposure values via direct soil ingestion. In addition, the authors suggest that REE bioaccessibility in food is reduced due to the presence of organic complexes, such as phytates. These results are relevant, since bioaccessibility studies performed for other elements show evidences to conclude that an over-estimation of risk can occur if the risk evaluation considers only the total contents [164, 165]. Adding to this, there is also the need for speciation studies, in order to identify the soluble and insoluble species for each soil environment [79, 157].

Thus, additional experiments that seek to evaluate the real contents to which human beings are exposed to REE are an urgent need. These results could possibly reduce the pressures imposed mainly on agriculture, which is the main activity (as a diffuse source) responsible for increasing the contents of REE in soils [53], due to either REE direct (China) or indirect use (other countries). Knowing several bioaccessibility scenarios for these elements would allow decision-making with higher safety.

In the absence of these researches, analyses of “case studies” can allow, in a preliminary manner, to associate exposure conditions to their effects. Table 5 shows some of these studies. It is verified that hair, blood, and urine can be used as exposure indicators. Populations exposed to elevated REE contents can present alterations in these parameters. Table 5 also shows studies that can help to evaluate ecological risks.

Regarding ecological risk evaluations, it cannot be affirmed if there is or there is not risk in a generalized manner. Each scenario must be specifically evaluated, taking the intrinsic variability of each environment into consideration, as well as the evaluation objectives, target organisms, among others [172].

It is known that REE toxicity is variable, depending on toxicological parameters and the target organisms [157]. Besides this, the chemical forms of REE compounds primarily determine deposition and retention of REE following the different routes of exposure [156]. Tables 6 and 7 show LD₅₀ values (lethal dose to 50 % of exposed individuals) for some REE through different administration routes. These data reinforce the need to evaluate bioaccessible contents, particularly when taking into consideration the great differences found between different routes of exposure, e.g., oral versus intravenous.

With the purpose of evaluating ecological risk, part of the information shown in Table 3, which report selected adverse effects of REE in plants (and their respective concentrations), could be used to construct a database that allows the elaboration of mathematical models to estimate safe doses of REE in soils. However, the existence of a limited number of studies in this subject, as well as others

Table 4 Provisional reference doses (p-RfD) for selected REE.

Element	p-RfD (mg kg ⁻¹ day ⁻¹)
Europium (chloride)	0.03
Europium (oxide)	0.002
Lanthanum (carbonate) ^a	0.5
Lanthanum (chloride)	0.005
Lanthanum (oxide)	0.02
Lutetium(chloride)	0.0009
Neodymium (chloride)	0.5
Praseodymium (chloride)	0.5
Samarium (chloride)	0.5
Samarium (nitrate)	0.00002
Scandium (oxide)	0.005
Yttrium (chloride)	0.004

Source: [160–163]

^a This value was not considered provisional

Table 5 Ecological and human health risk assessment indicators for REE

Element	Media	Effect	Concentration	Source
REE	Agricultural soils near a REE-mining area	Intake of REE from vegetables did not exceed safe values (100–110 $\mu\text{g kg}^{-1} \text{ day}^{-1}$), i.e., low risk to human health due to ingestion of food containing REE. Positive and significant correlation between soil-REE and blood-REE ($R^2 = 0.6556$; $p < 0.05$). Soil-REE contents increased by 29.5 % near mining sites when compared to background contents of soils from China (187.60 mg kg^{-1}).	$\Sigma \text{REE}_{\text{soil-total}} = 135.85\text{--}327.56 \text{ mg kg}^{-1}$ $\Sigma \text{REE}_{\text{soil-bioavailable}} = 57.89\text{--}158.96 \text{ mg kg}^{-1}$ $\Sigma \text{REE}_{\text{vegetables}} = 0.07\text{--}64.42 \text{ mg kg}^{-1}$ $\Sigma \text{REE}_{\text{blood}} = 424.76\text{--}1274.80 \mu\text{g L}^{-1}$	[79]
REE	Population living near a REE-mining area	Hair-REE contents in women and men increased by 13 and 34 %, respectively Men accumulate about 22.5 % more REE in hair when compared to women living near the REE-mining site. Urine-REE contents increased by 332 % (compared with control). Addition of REE-fertilizer + urea increased nitrous oxide (N_2O) emissions to atmosphere in lowland and upland soils 21 and 19 % increase with 0.6 $\text{mg}_{\text{REE}} \text{ kg}^{-1} + 0.15 \text{ g urea kg}^{-1}$; 104 % and 60 % increase with 6.0 $\text{mg}_{\text{REE}} \text{ kg}^{-1} + 0.15 \text{ g urea kg}^{-1}$ for lowland and upland soils, respectively.	$\Sigma \text{REE}_{\text{hair women-mining site}} = 209.82\text{--}3178.83 \text{ ng g}^{-1}$ $\Sigma \text{REE}_{\text{hair men-mining site}} = 238.4\text{--}3460.03 \text{ ng g}^{-1}$	[166]
REE	Population living near a REE-mining area		$\Sigma \text{REE}_{\text{urine-control}} = 0.265 \mu\text{g g}^{-1} \text{ creatinine}$ $\Sigma \text{REE}_{\text{urine-mining site}} = 0.881 \mu\text{g g}^{-1} \text{ creatinine}$	[167]
La, Ce, Pr, Nd, Sm	Agricultural soil		REE-fertilizer: La_2O_3 28 %; CeO_2 50.8 %; Pr_6O_{11} 15.8 %; Nd_2O_3 15.8 %; Sm_2O_3 0.1 %	[168]
La, Ce, Nd, Pr, Sm, Eu, Gd, Tb, Dy, Y	Soils near a REE-mining area	Soil-REE contents increased up to 27,316 mg kg^{-1} near mining sites, when compared with control. Soil contamination with REE decreased population of Carabida and Dermaptera but did not affect Formicidae.	$\Sigma \text{REE}_{\text{soil}} = 233.20\text{--}27,549.58 \text{ mg kg}^{-1}$	[169]
REE	Agricultural soil	Contents of REE (as oxides) in orange pulp (0.016–0.125 mg kg^{-1}) did not exceed safe levels (0.7 mg kg^{-1} fresh weight).	$\Sigma \text{REE}_{\text{soil}} = 38.6\text{--}546.0 \text{ mg kg}^{-1}$ $\Sigma \text{REE}_{\text{Orange pulp}} = 0.106\text{--}0.828 \text{ mg kg}^{-1}$	[170]
La, Ce, Y	Artificial soil	Positive relationship between REE contents in soils and orange fruit quality (acidity, soluble solids, and vitamin C). La, Ce, and Y may reduce germination and plant yield, especially after exposing them to Ce at low soil pH.	$\text{La} = 4.4\text{--}396.5 \text{ mg kg}^{-1}$ $\text{Ce} = 25.7\text{--}1209.9 \text{ mg kg}^{-1}$ $\text{Y} = 10.2\text{--}910.6 \text{ mg kg}^{-1}$	[171]

Table 6 Acute intraperitoneal, oral, and intravenous toxicity of rare earth nitrates to female/male mice and rats (LD₅₀)

REE	Intraperitoneal		Oral	Intravenous	
	Female mice mg kg ⁻¹	Female rats mg kg ⁻¹		Female rats mg kg ⁻¹	Male rats mg kg ⁻¹
Lanthanum	131	–	–	–	–
Cerium	151	93	1355	1.4	16
Praseodymium	94.4	79	1134	2.4	25
Neodymium	89	89	905	2.1	22
Samarium	106	96	901	3	20
Europium	109	72	>1704	–	–
Gadolinium	105	80	>1743	–	–
Terbium	168	91	>1753	–	–
Dysprosium	110	105	1103	–	–
Holmium	115	97	1078	–	–
Erbium	81	83	–	13	19
Thulium	93	104	–	–	–
Ytterbium	93	94	1148	–	–
Lutetium	108	125	–	–	–

Source: [154]

involving several important ecological indicators (e.g., invertebrates, birds, etc.), reveals the big challenge that researchers still have in generating consistent information in order to evaluate the real effects of REE present in soils, over the most diverse target organisms that exist in the ecosystems.

Finally, it is worth mentioning that even though studies that evaluate REE effects in the environment can present relevant information in order to contribute to ecological risk evaluation, the comparison of existing studies is difficult due to methodological divergences [157]. Moreover, existing divergences between beneficial and adverse results can also be related to the doses used, which are not broad enough to overcome the controversy associated with the hormesis phenomenon [158].

Table 7 Acute intraperitoneal and oral toxicity of rare earth chlorides to male mice (LD₅₀)

REE	Intraperitoneal mg kg ⁻¹	Oral mg kg ⁻¹
Dysprosium	585	7650
Erbium	535	6200
Gadolinium	550	>2000
Holmium	560	7200
Samarium	585	>2000
Scandium ^a	440	–
Terbium	550	5100
Thulium	485	6250
Dysprosium	585	7650

Source: [155, 156, 173–175]

^a Intravenous = 24 mg kg⁻¹

Conclusion

Current uses of rare earth elements (REE) include automobile catalysts and petroleum refining, flat panel displays (cell phones, portable DVDs, TVs, and laptops), permanent magnets and rechargeable batteries for hybrid and electric vehicles, numerous medical devices, and in agriculture. Soil is a primary destination of most products/by-products containing REE; however, little is still known about the effects of REE in the soil environment, including effects on plants, animals, and humans. Indeed, despite the increasing number of studies with reference to REE in soils observed in the last 5–6 years, researchers worldwide are still trying to unveil the toxicological effects, as well as the possible benefits of REE to plants. Many questions about the biological role of REE remain unanswered. Even more uncertain and unexplored are models available for ecological and human health risk assessments. It is therefore important that we continue to advance with studies to better understand the effect of native/anthropogenic soil REE contents upon living systems, with special emphasis on cellular functions, nutrient uptake, and bio-accessibility. Increasing information on reference values for REE in soils worldwide has been available recently, yet their chemical behavior, speciation, and availability in the environment are not well known. Finally, studies concerning the use of REE in agriculture in order to increase crop yields should be further refined to understand the actual mechanism of action of these elements on cellular and physiological processes.

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Compliance with Ethical Standards

Conflict of Interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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