REVIEW

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Rare earth elements in plants

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Abstract

Since 1960, the positive effects of rare earth elements (REE) on crop physiology have been observed, and support for photosynthesis, biomass accumulation, secondary metabolites, or enzymes has been reported in 40% of studies. A higher content of chlorophylls *a* and *b* as well as carotenoids have been found along with an increased efficiency of photosystem II photochemistry and electron transfer rates. An increased activity of a key photosynthetic enzyme was also found in several plants growing in soil with a higher content of REE. An appropriate amount of REE also activates the antioxidant activity of peroxidase, superoxide dismutase, and catalase. These enzymes, together with a higher content of flavonoids and carotenoids, increase the resistance of plants to oxidative stress caused by different abiotic stresses. The positive effect of REE on biomass accumulation was also confirmed, but their affection on mycorrhizal symbiosis remains ambiguous. On the other hand, an excess of REE leads to damage to plants including the chloroplast ultrastructure. Therefore, the positive and negative effects of REE remain controversial, and the mechanisms of effects of REE in plants remain poorly understood. In addition to physiological processes, the absorption, bioavailability, and translocation of REE in plants as well as their possible ecotoxicology and hyperaccumulation are discussed in this review.

Additional keywords: antioxidants, carotenoids, chlorophyll, chloroplast, ecotoxicology, hyperaccumulators, mycorrhizal symbiosis.

Introduction

Global production of rare earth elements (REE) has increased exponentially in recent decades because of their applications in wind turbines, electric motors, catalysts, solar panels, mobile phones, batteries, laptops, lasers, fiber-optics magnetic resonance tomography, new drugs, *etc.* World production has more than doubled in the last 20 years. Peak production occurred in 2006, with more than 137×10^6 kg of rare earth oxides (REO) (Walters and Lusty 2011). Over the long term, China has dominated the global REE scene, accounting for approximately 95% of the total production (Jaireth and Hoatson 2014). Emissions from oil-fired plants, refineries, and mining practices are sources of pollution over long distances. Transport of air masses enriched with REE at a global scale has been reported since 1979. Increasing amounts of REE have been detected in several ecosystems (Tyler and

Olsson 2006). In addition to the various industries, the use of REE in agriculture has steadily increased. They are widely used as microfertilizers because lanthanides can increase crop yields. The area of fields with applied REE reached 160 - 290 thousand km² in 1995. Around 2005, REE consumption for agricultural purposes reached almost 100×10^9 kg per year. Moreover, REE are used as feed additives as they can improve the production of milk, eggs, and meat. However, an increased use of REE significantly increases pollution of ecosystems. In relation to this issue, the positive and negative effects of REE should be considered.

A positive effect of REE on crop production has been observed since 1960 (for review see El-Ramady 2008). Appropriate amounts of REE can promote plant growth and development because they have similar physiological

Submitted 16 November 2017, *last revision* 16 March 2018, *accepted* 21 March 2018.

Abbreviations: AM - arbuscular mycorrhizis, CAT - catalase; CEC - cation exchange capacity; Chl - chlorophyll; GOT - glutamic oxaloacetic transaminase; HREE - heavy REE; LREE - light REE; POD - peroxidase; PS - photosystem; REE - rare earth elements; REO - rare earth oxides; Rubisco - ribulose-1,5-bisphosphate carboxylase/oxygenase; SOD - superoxide dismutase.

Acknowledgments: This work was supported by project COST ES1407 (project No. LTC17046).

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effects as some mineral nutrients. In this review, we summarize up-to-date information about the role of REE in plants. An increase in plant biomass by stimulating

photosynthetic rate, an effect on plant resistance, and many other positive or negative effects of plants metabolism are described below.

What are rare earth elements?

Rare earth elements are trace metals that include the lanthanide group with 15 elements: 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 lutetium (Lu) with an increasing atomic number (57 to 71) in the periodic table. According to the International Union of Pure and Applied Chemistry (IUPAC) REE have similar physical and chemical properties, with even being magnetic and luminescent, and are often found in the same ore deposits except unstable Pm (Hatch 2012, Jaireth *et al.* 2014). The lanthanides are divided into two groups (Miao *et al.* 2008, Long *et al.* 2010, Walters and Lusty 2011): the light rare earth elements (LREE) with atomic numbers from 57 to 63 (La to Eu), and the heavy rare earth elements (HREE) ranging from 64 to 71 (Gd to Lu). Despite its low atomic mass, yttrium has properties more similar to the HREE and is often included in this group (Sneller *et al.* 2000). Compounds containing light lanthanides are considered more soluble than compounds containing heavy ones (Sneller *et al.* 2000). On account of their unique and diverse chemical similarity, the REE can very easily replace one element for another in crystal structures (Walters and Lusty 2011).

These elements are natural parts of the environment. Abundances of REE in soils are influenced by texture, weather history, pedogenic processes, organic matter content, and anthropogenic activities. More than 250 minerals containing REE are known (Walters and Lusty 2011). The REE occur naturally as oxides, silicates, carbonates, phosphates, and halogen compounds (Tyler 2004a, Jaireth *et al.* 2014). The LREE are more common, easily extracted, incompatible, and more concentrated in the continental crust than the HREE (Walters and Lusty 2011). Most geological events cause the redistribution of REE changing the LREE/HREE ratio (Fu and Akagi 1998). Nevertheless, the occurrence of LREE is generally

higher than HREE as it follows the Oddo-Harkins rule. According to this rule, elements with even atomic numbers are more abundant than their neighbours with odd atomic numbers because of their greater relative stability of atomic nuclei (Jaireth *et al.* 2014). In the earth crust, the content of REE in soils in mining areas or mine tailings also obey the Oddo-Harkins rule (Sneller *et al.* 2000, Miao *et al.* 2011, Walters and Lusty 2011, Aide and Aide 2012, Anawar *et al.* 2012, Gonzalez *et al.* 2014, Jaireth *et al.* 2014).

The term “rare” does not refer to the relative crustal abundance of these elements (Walters and Lusty 2011) but to the absence of concentrated REE in a pure ore deposit as other elements (*e.g.*, gold) (Gonzalez *et al.* 2014). The total content of REE increases from 11 to 12 mg kg⁻¹ in the lower crust up to ~170 mg kg⁻¹ in the upper crust. Rare earth elements are concentrated in the earth's crust in substantial quantities, but they are widely dispersed and present in smaller quantities near the earth's surface (Dobrinsky 2013). The total content of REE ranges from 54 to 130 mg kg⁻¹ in the following order: Ce > La = Y > Sc > Nd > Sm > Pr > Gd > Dy > Eu > Tb > Er > Yb > Ho > Lu > Tm (Redling 2006). Since they have similar chemical and physical characteristics, the lanthanide elements and yttrium often occur together in nature and can be mined only together as co-products. Therefore, the recoverable amount of individual REO depends on the deposit composition (Polinares 2012).

The chemical nature of REE is a function of their atomic number (Merten *et al.* 2004). The most common valence for lanthanides is +3 when they are dissolved although some of them can be present in +2 and +4 oxidation states (Walters and Lusty 2011, Gonzalez *et al.* 2014). The Ce-anomaly is reported under oxidizing conditions, and typically trivalent ions Ce³⁺ are transformed to Ce⁴⁺ (>300 mV at pH 7). The Eu-anomaly usually occurs under reducing conditions; Eu³⁺ is reduced to Eu²⁺ (<-350 mV at pH 7).

Factors affecting REE absorption and transport

The uptake and transport of REE in plants have attracted attention during the last decade, but the available information on the soil-plant system enriched with REE is limited and fragmented (Wahid *et al.* 2003, Hu *et al.* 2004). With changing environmental conditions, understanding the biological impact of REE especially on natural plants is required. Nevertheless, the uptake, bioavailability, and translocation of REE within root systems are overlapping with the uptake and translocation

of other mineral nutrients.

Firstly, the adsorption and desorption of REE are affected by the physico-chemical properties of the soil (Wahid *et al.* 2003, Liang *et al.* 2005, Loell and Albrecht 2011, Miao *et al.* 2011, De Araújo *et al.* 2012): 1) Uptake of REE *via* roots is linked to Fe-oxyhydroxides in the rhizosphere (Brioschi *et al.* 2013, Durães *et al.* 2014); 2) The mobility of elements within the soil profile depends on the pH value of the rhizosphere and the redox

potential of the soil (Cao *et al.* 2001, Wu *et al.* 2001, Shan *et al.* 2002, Tyler 2004b, Durães *et al.* 2014); 3) Uptake of REE by plants tends to be higher at a low pH (Cao *et al.* 2001, Shan *et al.* 2002, Tyler 2004a); 4) Biochemical cycling and fractionation of REE in soil resulting from atmospheric deposition (Stille *et al.* 2009); 5) The cation exchange capacity (CEC) of soil is an important factor affecting the adsorption and desorption of (not only) REE (Jones 1997, Shan *et al.* 2002, Shan *et al.* 2003b); 6) The plant uptake rate is dependent on the valence of an element (Tyler 2004b); 7) The Casparian stripes in plant root endodermis limit uptake of REE (Hu *et al.* 2004, Brioschi *et al.* 2013); 8) Complexes formed by low-molecular-mass-organic acids and other plant root exudates predict the bioavailability of REE (Fu *et al.* 2001, Zhimang *et al.* 2001, Shan *et al.* 2002, 2003a,b); 9) Organic and inorganic ligands play an important role in REE absorption by plant roots and fractionation of REE (Fu *et al.* 1998, 2001, Zhimang *et al.* 2001, Shan *et al.* 2003b, Ding *et al.* 2005, 2007, Liang *et al.* 2005, Ma *et al.* 2008, Zanin and Zamirailova 2009, Durães *et al.* 2014); 10) The addition of fulvic, humic, malic, and citric acids, histidine, or ethylene diamine tetraacetic acid (EDTA) changes bioaccumulation of REE in plants as metals complexed with, *e.g.*, fulvic acids, are more available to plant roots (Zhimang *et al.* 2001, Shan *et al.* 2003a, Ding *et al.* 2005, Liang *et al.* 2008); 11) The affinity of plasma membrane affects absorption of individual elements (Hu *et al.* 2004); 12) Chelators (aspartic acid, asparagine) may have a positive effect on uptake of REE (Wu *et al.* 2013); 13) Uptake of REE may be facilitated by an increased nitrogen and potassium fertilization and decreased by addition of phosphates (Hu *et al.* 2004).

Roots preferentially absorb LREE below 50 cm soil depths (Stille *et al.* 2009, Brioschi *et al.* 2013, Durães *et al.* 2014). The bioavailability of compounds to plants represents one of the most important issues for environmental studies. Studies have indicated the importance of speciation and complexing REE with various ligands under different pH. Rare earth elements complexation with carbonate ions predominates in the majority of natural waters of moderate to high pH where carbonates are the major component (Johannesson and Lyons 1995). Speciation calculations showed that REE-carbonate complexes dominate and typically account for more than 99% of each rare earth element in solution. In almost neutral pH ($7 \leq \text{pH} \leq 9$), the inorganic speciation of the REE in complexes with carbonate includes LnHCO_3^{2+} , LnCO_3^+ , and $\text{Ln}(\text{CO}_3)_2^-$, and that with phosphate $\text{LnH}_2\text{PO}_4^{2+}$, LnHPO_4^+ , $\text{Ln}(\text{HPO}_4)_2^-$, and LnPO_4 . In water with a low pH ($\text{pH} < 6.5$), free metal ions dominate the speciation of REE (Johannesson *et al.* 1996).

Other extremely important soil variables that influence bioavailability include redox potential, soil texture, and organic matter content (Cao *et al.* 2001). Interactions among elements and compounds influence availability *via* antagonistic or synergistic mechanisms as

chemically similar elements may compete for the same binding sites (*e.g.*, Ca and REE) (Thomas *et al.* 2014). Rare earth elements release increases with the decrease of pH, solubility is comparable under the same redox potential, but REE release is enhanced when redox potential decreases within the same pH values. It seems that the mobilities of La, Gd, and Y depend mainly upon pH value, whereas the release of Ce depends both upon pH and upon redox potential. Rare earth elements release is positively correlated with the release of Fe and Mn (Cao *et al.* 2001). Adsorption capacities of REE are significantly correlated with CEC of soils. The CEC is probably also related to humic acid content as Gu *et al.* (2001) found a significant linear relationship between humic acid and CEC. Generally, CEC, redox potential, mobility, and subsequent availability of rare earth element cations in the soil increase at a lower pH (Shan *et al.* 2002, Thomas *et al.* 2014).

Rare earth elements uptake by plants is not only controlled by the plant itself but depends on their content in soil, soil water pool, and other minerals (Weltje *et al.* 2002, Brioschi *et al.* 2013). Water-soluble and exchangeable fractions of REE are the most available (Li *et al.* 1998, Cao *et al.* 2000, Xu and Wang 2001, Zhang and Shan 2001, Redling 2006). Other sources include silicate particles in soil (Fu *et al.* 2000, Fu *et al.* 2001) and airborne particles (averaging less than 2.5 μm) or gasses absorbed by vegetation (Sun and Zhao 1994, Peresedov and Gundorina 1997).

There are two different options for REE distribution patterns in an ecosystem: a distribution pattern in plants and a distribution pattern in soil. The amount of REE in plants is not correlated with the content of REE in the rhizosphere (Wytenbach *et al.* 1998, De Araújo *et al.* 2012, Durães *et al.* 2014) either due to a greater control of REE uptake by plant properties (Tyler and Olsson 2005). Nevertheless, a significant linear correlation between soil REE content and corresponding leaf or root REE content in palms growing in a sandy soil has been observed (Wahid *et al.* 2003). and also similarities in distribution patterns of REE between soil and seeds were observed (Wytenbach *et al.* 1994, Liang *et al.* 2005). Nevertheless the process of REE transportation and accumulation by plants is influenced by different REE biogeochemical characteristics, *e.g.*, of goldfields. *Pinus massoniana* grown in the gold mineralization zone transports REE to the aboveground parts more efficiently comparing to the background areas. (Miao *et al.* 2011). By contrast, higher amounts of REE (3 to 7 times higher) are consistently found in the rhizosphere than in trees (oak, spruce, and beech) (Brioschi *et al.* 2013) and natural plant vegetation samples (Durães *et al.* 2014). There are huge differences in REE content in herbaceous plants but with no clear relationship between REE in leaves and REE soil content.

Light rare earth elements are more mobile and preferentially exported by surface and subsurface runoff, which also implies that LREE are more available for root absorption than HREE (Ozaki *et al.* 2000, Hagerberg and Thelin 2003, Brioschi *et al.* 2013). This enrichment is

probably related to a higher mobility of LREE in the soils mentioned above and amplified by a higher stability of dissolved HREE complexes in soil water. Roots preferentially absorb free ions rather than dissolved complexes (Brioschi *et al.* 2013). The actual fractionation of REE reflects a tendency toward a decreasing transfer of REE with increasing atomic mass and decreasing ionic radius (Tyler and Olsson 2005). Uptake of non-essential ions, their retention in roots, and redistribution into specific organs are species-specific and depend on the metal resistance mechanisms of the species (Närhi *et al.* 2014) and properties of the endodermis. Moreover, REE are potentially associated with different development stages (Brioschi *et al.* 2013, Durães *et al.* 2014). A positive correlation between LREE amounts and Fe-oxyhydroxides in bedrock and soil was found. Content of REE in tree roots can correlate with Fe-Mn-oxyhydroxides content in the limestone soils with Fe-oxyhydroxides in the clay-humus soil. Plants seem to use the same mechanisms applied for the micronutrient Fe to absorb REE (Brioschi *et al.* 2013).

A strong relationship between plants and silicon seems quite natural due to its substitution in the soil. Moreover, REE and Si are concentrated in silicate rock, and oxides of REE are very stable as lithophilic elements. There is a linear accumulation of REE as well as Si in Norway spruce (*Picea abies*) (Wytenbachet *et al.* 1994). By contrast, a strict relationship between them even within the same tissue of different species or within tissues from a single species has not been found in other tree species (Fu *et al.* 2001).

Bioaccumulation and plant hyperaccumulators: Plants take up a wide range of mineral nutrients including REE. Some plantspecies are able to accumulate metal and metalloid trace elements in their biomass in considerably higher amounts in comparison to other species; *e.g.*, *Sebertiaacuminata* from New Caledonia contains 25 % of nickel in dry latex. A high accumulation of metals within plant tissue without a strong negative impact on growth, development, or reproduction is called hyperaccumulation. Understanding uptake, transfer, and storage of metals in hyperaccumulators lies at the interface between geochemistry and plant physiology (Wang *et al.* 2003). Moreover, hyperaccumulators as well as common plants can solubilize REE in soil (Shan *et al.* 2003a,b). Accumulation of lanthanides seems to be a characteristic of *Pteridophyta* (De Araújo *et al.* 2012). Typical examples of REE hyperccumulators are *Dicropeteris dichotoma* and *Pronephrium simplex*. The content of LREE in dry mass of leaves of *D. dichotoma* is approximately 0.7 % (Shan *et al.* 2003a), and *P. simplex* accumulates REE in lamina up to 1.2 mg g⁻¹(d.m.) with a higher affinity to LREE (Lai *et al.* 2006). Also fern *Alsophila sternbergii* is mentioned among species with a high ability to accumulate LREE (De Araújo *et al.* 2012). Concentration ratio defined as the quotient of plant tissue/substrate) elemental concentration (Wahid *et al.* 2003), or transfer factor (TF=C_{plant}/C_{soil}) can be used to describe the ability of

plants to accumulate REE in the plant biomass. *Pachystroma longifolium* (França *et al.* 2002), *Sphagnum* sp. (Markert and De Li 1991) and even citrus can be considered as bioaccumulators. The leaf/soil ratio of La (0.62-1.09) makes citrus even a stronger bioaccumulator than the two aforementioned plants (Turra *et al.* 2013). As described above, a larger pool of total REE in soil is usually reflected in higher amounts of REE in plant tissue, up to, *e.g.*, 9 880 ng g⁻¹(d.m.) in *Populus sieboldii* (Fu *et al.* 2001) and 10.1 nmol g⁻¹(d.m.) in *Anemone nemorosa* (Tyler and Olsson 2005). Three species (*Carlina corymbosa*, *Erica australis*, and *Lavandula luisierrae*) growing on mine tailings can accumulate high amounts of REE [La 0.45 - 0.57, Ce 0.68 - 2.41 mg kg⁻¹(d.m.)] (Anawar *et al.* 2012).

Aspartic acid and asparagine promote the remediation capabilities of the hyperaccumulator *Phytolacca americana* when used as a chelator (Wu *et al.* 2013). In *Lycopersicon esculentum*, application of aspartic acid and asparagine enhances La absorption into roots, whereas application of glutamic acid and histidine affects La translocation from roots to shoots (Wu *et al.* 2013). These findings have important implications for the phytoremediation of REE contamination in soil.

The importance of mycorrhizal fungi: Mycorrhizis acts as one of the most important factors influencing the availability of REE to plants. Root exudates with fungal hyphae and roots promote mineral acquisition and dissolution in the rhizosphere (Tyler and Olsson 2005). Acid and chelating compounds are released into the soil to dissolve phosphate minerals, silicate particles, and others sources of REE (Fu *et al.* 2001).

Endomycorrhizal fungi, especially arbuscular mycorrhizal (AM) fungi can improve biotic and abiotic stress tolerance of its host plant. They enable uptake of mineral nutrients including REE, but they can also act as a barrier to REE. The content of REE in sporocarpsis similar or higher than in host plants in dependence of soil properties (Aruguete *et al.* 1998). In ectomycorrhizal fungus, calcium ions can be substituted by lanthanide ions (Aruguete *et al.* 1998).

An increasing La accumulation in *Astragalus sinicus* is associated with an increasing content of La in soil regardless of mycorrhizal or non-mycorrhizal treatment. In comparison to other plants, in maize and sorghum, AM colonization significantly reduces La content in shoots and roots (Guo *et al.* 2013). Application of higher La doses [5 mg kg⁻¹(soil)] decreases activity of succinate dehydrogenase (SDH) and alkaline phosphatase (ALP) in fungal mycelium. These two enzymes are considered as an indicator of AM fungi colonization (Chen and Zhao 2007).

Treatment with AM fungi significantly increases N, P, and K content in shoots and roots of *Astragalus sinicus* and growth of *Zea mays* and *Sorghum bicolor* in soil enriched with REE. Dry masses of the investigated plants increase by 211 to 387% in shoots and roots compared with the non-inoculated treatment (Chen and Zhao 2009,

Guo *et al.* 2013). An AM fungus colonization might be effective for mitigation of La toxicity by significantly improving P content in shoots and roots and therefore the amount of plant biomass (Chen and Zhao 2007).

Rare earth elements content in plants affect inoculation of fungi on roots. Seedlings of *Pinus sylvestris* accumulate REE in roots 16 - 23 times more than in shoots, but this process is dependent on the inoculated fungi (Hagerberg *et al.* 2003, Chen and Zhao 2007). The effect of mycorrhizal fungi colonization on plant REE uptake probably depends on plant species, substrate, species of fungi, and concentration of REE.

Heavy metal toxicity to plants is strongly affected by the amount of REE in soil due to their synergic effects. However, amelioration of heavy metal toxicity is possible by a low concentration of REE. A significant decrease in content of certain heavy metals in shoots and roots has been observed in *Zea mays* and *Sorghum bicolor* inoculated with AM fungi. Glomalin produced by AM fungi can decrease metal toxicity by reducing metal absorption and enhancing plant tolerance (Hildebrandt and Regvar 2007, Guo *et al.* 2013).

Absorption and transport within a root system: Low molecular mass organic acids are important root exudates; they can be produced as a consequence of plant protein decomposition (Shan *et al.* 2002). Due to their metal-chelating and/or complexing properties, they can influence metal solubility in soils and uptake by plants (Shan *et al.* 2002, 2003a,b). However, adsorption and desorption of REE from soil are closely related to the stability of complexes formed between REE and root exudates. Nevertheless, for citric, malic, and tartaric acids, adsorption of REE decreases to varying extent in comparison to nitrates and acetic acid. The suppression of REE adsorption follows the order citric acid > malic acid > tartaric acid > acetic acid consistently with the order of stability of the complexes of REE with these organic acids (Shan *et al.* 2002).

Organic acids, redox potential, and soil pH are important factors affecting REE bioavailability (Shan *et al.* 2002, 2003b). Although the relationship between REE desorption and soil pH is complicated and depends, *e.g.*, on soil acid type, desorption of REEs decreased with increasing equilibrium solution pH (Shan *et al.* 2002). Organic acids (citric and malic acids) and histidine alter accumulation of REE in plants depending on the soil type (Shan *et al.* 2002, 2003a). Increasing content of organic acids increase desorption of REE (Shan *et al.* 2002). Nevertheless, the promotion of REE uptake from soil with a low pH can be observed. Histidine and organic acids promote uptake and sequestration of LREE in *Dicranopteris dichotoma* leaves (Shan *et al.* 2003a). Low concentrations of fulvic acid (FA) in wheat increases

bioaccumulation of REE in different parts of the plant. Adding increasing or high concentrations of FA (Zhimang *et al.* 2001), EDTA (Ding *et al.* 2007), and citrate changes glutamic oxaloacetic transaminase (GOT) activity and so decrease bioaccumulation of REE (Zhimang *et al.* 2001). Different changes in LREE and HREE content in leaves is observed with increasing content of EDTA and Ca^{2+} (Ding *et al.* 2007).

In addition, physicochemical properties of soil, such as organic matter, iron, manganese, and aluminum oxides, affect the bioavailability of REE to plants. The absorption capacity of REE is even significantly correlated with the cation exchange capacity of soil (Shan *et al.* 2002).

Glutamic oxaloacetic transaminase and tetrad effect:

Variations in GOT activity provide important information on the REE bioavailability and accumulation in the plant body. In plants, GOT activates nitrogen and amino acid metabolism. A correlation between bioaccumulation of REE in roots and shoots and GOT activity has been demonstrated in *Dicranopteris dichotoma* and *Triticum aestivum* (Zhimang *et al.* 2001, Wang *et al.* 2003).

A valuable indicator of the distribution pattern of REE among organs or tissues in the plant body seems to be the tetrad effect or concentration ratio (Wahid *et al.* 2003). The tetrad effect can cause partitioning chondrite-normalized REE patterns, where chondrite normalized means ratio of La_2O_3 and La. The ratios of samples and chondrite are plotted on a logarithmic scale against the atomic number into four segments called tetrads (the first tetrad, La-Ce-Pr-Nd and the fourth tetrad, Er-Tm-Yb-Lu). The tetrads form W or M shape after connection of all REE normalized concentration in the graph (Masuda *et al.* 1987). The tetrad effect has been described for dicotyledons, monocotyledons, gymnosperms (Fu *et al.* 2001, Ding *et al.* 2005, Ding *et al.* 2007, Durães *et al.* 2014), and ferns (Fu *et al.* 1998), and the REE tetrads shape in different plant organs can provide useful information about REE transportation in the environment (Masuda *et al.* 1987, Ding *et al.* 2005, 2007).

In nature, citrate plays a very important role in altering REE bioavailability by complexation with REE in soil (Ding *et al.* 2005). The amount of ligand affects REE patterns in different parts of a plant (Fu *et al.* 2001).

A higher affinity between REE and inorganic ligands, such as phosphate (PO_4^{3-}), plays important roles in REE bioaccumulation (Ding *et al.* 2005, Liang *et al.* 2008). Generally, the amount of REE in leaves decreases with increasing amount of applied phosphate, but no changes in REE occur in wheat roots (Ding *et al.* 2005). A similar result is achieved in soybean: Next to the Pi (as an anorganic ligand) REE fractionation is influenced by cell wall absorption (Ding *et al.* 2007).

Distribution of REE in plants

Location of REE in the intra- and extra-cellular space: Understanding the REE localization in plant tissues is very important (Hu *et al.* 2004). The largest amount of REE (68%) is presented as REE-pectin complexes in cell walls (Lai *et al.* 2006). A large amount of Ca^{2+} is stored in the cell wall as calcium pectinate. Nevertheless, carboxyl groups of pectin acid which have not been esterified provide many binding sites for metal ions (Lai *et al.* 2006). The lanthanides are able to substitute for Ca^{2+} as they are approximately of the same size as Ca^{2+} . Moreover, their trivalency gives them a much higher charge to volume ratio so that they usually have much higher affinities than Ca^{2+} for the given binding sites (Evans 1983). Due to the chemical properties of lanthanides the plant physiology could be changed by Ca^{2+} regulation on the cellular level (Zeng *et al.* 2000, Tyler and Olsson 2005, Durães *et al.* 2014).

A high affinity of La^{3+} to the cell wall might be one possible reason for its increased uptake by ferns. Addition of Ca^{2+} and especially of La^{3+} accelerates growth of *Dryopteris erythrosora*. Rare earth elements are absorbed to a higher degree in comparison with other non-essential elements. The La^{3+} and Eu^{3+} can be absorbed by plant cells and bind to the membranes of chloroplasts, mitochondria, cytoplasm, and nucleus (Gao *et al.* 2003). Since the ratio of charge to the ionic radius of REE is higher than that of Ca^{2+} , REE may have a higher ability to bind to pectic acid in the chloroplast of *Pronephrium simplex*. Rare earth elements are distributed almost equally in the chloroplast membrane and thylakoids, and most REE in the thylakoids are bound to photosystem (PS) II complex (Lai *et al.* 2006). Thus, it is also possible that REE can replace Ca^{2+} and bind to PS II protein (Wang *et al.* 2003).

Apoplastic and symplastic pathways, xylem sap: Light rare earth elements accumulate in the cell wall, intercellular space, plasmalemma, vesicles and vacuoles of root endodermis and stele cells but not in the Casparian strips (Shan *et al.* 2003a). Apoplastic and symplastic pathway mechanisms of REE transport have been identified (Shan *et al.* 2003a). Along the apoplastic pathway, REE are passively transported through the cell wall according to a concentration gradient and do not cross the plasma membrane. In the symplastic pathway, solutes are transported across the plasmalemma. Both the apoplastic pathway and the symplastic pathway are interrupted by the endodermis with the Casparian strips (Lehmann *et al.* 2000, Shan *et al.* 2003a). A ion-selective cell wall located in the endodermis modifies or blocks transfer of specific ions. A huge difference in REE content between roots and other parts of a plant body is just caused by the endodermis. In some special roots, such as the nodal roots of *Hordeum vulgare*, the role of endodermis largely performs the exodermis (Lehmann *et al.* 2000). Deposits of LREE are observed in the phloem and xylem of the rhizomes (Shan *et al.* 2003a,

Brioschi *et al.* 2013). Nevertheless, the majority of REE (97%) in the xylem sap of soybean are combined with certain ligands (Ding *et al.* 2007).

The LREE and HREE layout varies according to the type of plants, but there is usually a slight enrichment of HREE in roots, confirming the reduced ability of plants to translocate HREE (Ding *et al.* 2007). Stems and leaves are enriched with LREE (Brioschi *et al.* 2013, Durães *et al.* 2014). The leaf position and its area differ in transpiration stream bulk which in return influences the fractionation between HREE and LREE within a plant. The HREE are preferentially transported with transpiration stream, leading to corresponding changes among different stem segments (Ding *et al.* 2007).

Cerium and europium anomaly: The anomaly described in several species is based on their lower or higher content in soil solution in comparison to other REE due different oxidation states (described above). Variations of different redox potential or the pH of soils can influence adsorption mechanisms. Generally, the REE pattern are comparable between plant organs and rhizosphere. Ce dominates in leaves and roots but it is depleted in stems relative to other REE (Fu *et al.* 1998, Brioschi *et al.* 2013, Durães *et al.* 2014). Cerium has a negative anomaly with respect to soil in *Picea abies*, *Abies alba*, *Acer pseudoplatanus*, *Hedera helix*, *Rubus fruticosus*, *Dryopteris filix-mas*, *Taxodium japonicum*, *Populus sieboldii*, *Sasa nipponica*, *Tea sinensis*, and *Vicia villosa* (Wytenbach *et al.* 1998, Fu *et al.* 2001). The conditions leading to the Ce anomaly are not uniform as demonstrated by the different sizes of the anomaly in the various species and by its variation between individuals of one species. Small changes in the redox potential of the rhizosphere might contribute to this variability (Wytenbach *et al.* 1998). Sap samples are additionally characterized by positive Ce anomalies, suggesting that REE may be associated with colloidal Fe-oxyhydroxide particles (Brioschi *et al.* 2013).

The Eu anomaly is dependent on the soil type. Limestone soils show strong positive Eu anomalies. A slight positive Eu anomaly occurs in granite soils, whereas no significant anomalies are found in carbonatite soil (Brioschi *et al.* 2013). The Eu anomaly is greater in roots and leaves than in stems, probably because of participation in metabolic functions due to similarity with calcium in membrane channels. The Eu anomaly is also well described in some crops, especially in stems and grains (Ding *et al.* 2006).

Fractionation of REE within plants: The REE content pattern called the fractionation is soil > roots > leaves (needles) > stems (trunks) > grains (seeds) in trees (spruce, beech, oak, and pine) and fern (*Matteuccia*) under natural conditions, and in wheat, rice, and vegetables after application of a REE fertilizer (Sun *et al.* 1994, Fu *et al.* 1998, Wen *et al.* 2001, Miao *et al.* 2011,

Brioschi *et al.* 2013). A hyperaccumulator *Dicranopteris dichotoma* follows the pattern leaves > roots > stems (Miao *et al.* 2011). The content of REE in plants was found higher in a mining area than in a non-mining area (Wang *et al.* 2006, Nazreen *et al.* 2017). Other results indicate that the total REE content in roots and stems is lower than in leaves because translocation of REE occurs in roots and stems (Miao *et al.* 2011). However, REE in *Populus sieboldii* follow the pattern leaves > main roots > trunks (Fu *et al.* 2001), and in *Citrus sinensis* budded on *C. limonia*, the pattern soil > leaves > peel > pulp > seeds > juice (Turra *et al.* 2013).

Different REE patterns may reflect a different mobility of REE in plants (Fu *et al.* 2001, Khan *et al.* 2017, Mikolajczak *et al.* 2017), but there is no clear correlation between increasing or decreasing accumulation and atomic number (Gonzalez *et al.* 2014).

Impact of REE on plant anatomy and physiology

Leaf anatomy, stomatal conductance, and transpiration rate: Reports on these topics are very rare. Rare earth elements are clustered in the cell wall, cytoplasm, and chloroplasts in leaf epidermal and mesophyll cells (Wang *et al.* 2006). The effect of yttrium has been described in young maize plants, but a synergic effect with other REE is missing. The presence of Y (10 mM) reduced maize growth and the length and width of stomata. Those changes are more pronounced on the abaxial than adaxial epidermis and contribute to prevention of water loss. The total leaf area declines, which might explain an increase in stomata density. Transpiration rate, stomatal conductance of water vapor, and water content also decrease (Maksimović *et al.* 2014). Stomatal conductance and leaf water potential of maize seedlings consistently decline with an increasing Y dosage from 0.05 to 0.5 mg g⁻¹(dry soil). Moreover, an appropriate dosage of Y of 0.05 mg g⁻¹(dry soil) improved water use efficiency (Maksimović *et al.* 2014).

Photosynthesis: There are only a few reports concerning the effects of REE on photosynthesis. The Ce³⁺, Nd³⁺, and La³⁺ promote growth and increase the Chl content and photosynthetic rate (Hong *et al.* 2002, Fashui and Xuefeng 2003, Hong *et al.* 2005). Treatments with Ce³⁺ increase fresh and dry masses, photosynthetic rate, and synthesis of Chl in *Spinacia oleracea* (Fashui and Xuefeng 2003, Hong *et al.* 2005). Further, REE can promote photosynthesis and crop yield by regulating ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) activity (Chen *et al.* 2000, Hong *et al.* 2005, Liu *et al.* 2007) and by improving light energy transfer from PS I to PS II (Liu *et al.* 2007). In the Chl molecule, La³⁺ may substitute for Mg²⁺ when there is lack or absence of Mg²⁺ in solution (Evans 1983, Hong *et al.* 2002). Deposits of REE are found in chloroplasts of intact mesophyll cells, mainly in thylakoid grana of *Dicranopteris dichotoma* and *Spinacia oleracea* (Shan *et al.* 2003a, Lai *et al.* 2006,

Nevertheless, Tyler and Olsson (2006) published the presumption that uptake from atmospheric deposition is positively related to a high ionic charge and atomic mass. There is some deflection in the absolute amount of elements during a growing season in leaves of *Fagus sylvatica* depending on their ionic charge. The amounts of REE in leaves of beech increase during early summer, stay almost the same during middle summer to autumn, and increased strongly in winter by direct passive uptake from atmospheric deposition (Tyler and Olsson 2006). The content of elements in soil and plant tissues decreases in the order Ce > La > Nd > Pr > Gd > Sm (Emmanuel *et al.* 2010a,b, Wahid *et al.* 2003) with the exception of La being slightly more abundant than Ce in leaves (Wahid *et al.* 2003). Other authors reported the order Ce > La > Pr > Nd in fern (Shan *et al.* 2003a).

Wang *et al.* 2006). Next to the chloroplasts, the REE were deposit in the cell walls and vacuoles. Comparison of plants from mining and non-mining areas has shown that the content of Chl *a+b* and β -carotene is greater in plants from mining areas, but the Chl *a/b* ratio is similar. The reason of higher content of β -carotene may be associated with the demand for extra energy quenching when the chloroplast membrane is damaged. Due to the higher amount of photosynthetic pigments the efficiency of PS II photochemistry and electron transport rate are significantly enhanced in the plant leaves from mining areas (Wang *et al.* 2006).

One of the main limiting factors of photosynthetic rate is the amount and activity of the Rubisco. In *Nicotiana tabacum*, La³⁺ at low concentrations significantly promotes Rubisco activity *in vivo*, and lanthanides in the order Ce³⁺ > La³⁺ > Gd³⁺ (Ln³⁺) increase the activity of Rubisco *in vitro* (Chen *et al.* 2000). There is a presumption that Ln³⁺ can replace Mg²⁺ to form the active site of Rubisco during the activation process. In the Rubisco-La complex, La is bound to the oxygen atoms of amino acid residues (Chen *et al.* 2000). Experiments with spinach revealed that La³⁺ and Ce³⁺ treatments significantly accelerate the photosynthesis. The dry mass was also enhanced thus La³⁺ and Ce³⁺ treatments promote accumulation of organic substances (Hong *et al.* 2005). The mechanism by which REE increase the production of plant biomass is the promotion of photosynthetic carbon fixation by increased Rubisco activity. Rare earth elements also induce expressions of nuclear and chloroplast genes. Nevertheless, each individual element from REE can form a different complex with Rubisco, mainly the secondary structure of this complex is different (Hong *et al.* 2005).

Nearly a half of the total amount of REE in chloroplasts is associated with PS II in fern thylakoids, whereas only 6.4% of REE is found in the PS I fraction (Lai *et al.* 2006). Therefore, REE are randomly integrated

with Chl and mainly localized in the protein structure of the PS II system (Wang *et al.* 2003, Lai *et al.* 2006). In chloroplasts the REE are probably bind to the carboxyl and hydroxyl oxygen of glutamic or asparagic acid. (Wang *et al.* 2003). The La^{3+} significantly improves PS II formation and enhances electron transport rate. Moreover, appropriate amounts of Ce^{3+} positively affects absorption of light energy, its transformation, electron transport rate, and photophosphorylation (Fashui and Xuefeng 2003, Yang *et al.* 2005, Zhou *et al.* 2009).

The increase of photosynthetic rate of spinach by Ce^{3+} might be related to the changes in PS II as well as to the electron transport rate (Fashui and Xuefeng 2003). Promoting activity of PS II and oxygen evolving rate by Ce^{3+} is mentioned also by Liu *et al.* 2007.

In addition, Ce^{3+} treatment can improve light absorption and the excitation energy distribution in both photosystems in case of Pb^{2+} pollution. The Ce^{3+} treatment together with Pb^{2+} pollution can maintain the stability of the chloroplast membrane and improve photosynthesis (Zhou *et al.* 2009), even accelerate oxygen production (Liu *et al.* 2007). Further, Ce^{3+} treatment can protect chloroplasts from aging during long-term photooxidation in *Spinacia oleracea* as it can significantly decrease accumulation of reactive oxygen species. Moreover, it reduces the content of malondialdehyde and maintains stability of the membrane structure (Yang *et al.* 2005).

Secondary metabolism: Under natural conditions, plants are exposed to abiotic and biotic factors to stimulate production of secondary metabolites. Rare earth elements may act as elicitors to increase secondary metabolite synthesis (Wu and Wang 2001). Antioxidants can protect plants against reactive oxygen species, which accumulate during stresses. The antioxidants include, *e.g.*, superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase, ascorbate, and glutathione. The enzymes CAT, peroxidase (POD), and phenylalanine ammonia lyase are activated by REE at low concentrations (0 - 200 μM), but when the concentration of REE exceeds 300 μM , the

enzyme activities decrease significantly. Expressions of some POD isozymes are inhibited, however, some other new POD isozymes are induced by REE. Another study suggested that REE increase POD and SOD activities as well as carotenoids and phenol content in cucumber (Emmanuel *et al.* 2010a,b). Treatment with REE can increase SOD, CAT and POD activities of aged rice seeds (Hong *et al.* 2000). Similar to heavy metals, REE inhibit the enzyme activities when their concentrations exceed a critical value. For example, esterase activity increases by adding 50 - 100 μM of REE but decreases by 200 μM REE (Xin *et al.* 2013). Under an acid rain, REE can significantly reduce the sensitivity of antioxidant enzymes to acid stress (Yan *et al.* 1999).

Another effect of REE, in this case lanthanum nitrate treatment, decreases free-radical production rate and peroxidation of membrane lipids in rice seeds (Fashui and Zhenggui 2000). A monazite soil (soil containing REE) significantly increases POD and SOD activities as well as activities of amylase and nitrogenase. Increased enzyme activities in the presence of REE influence nodulation, coleoptile formation, and biomass production in *Arachis hypogaea* (Emmanuel *et al.* 2010a,b).

Biosynthesis of certain secondary metabolites supported by REE, *e.g.*, taxol (Wu *et al.* 2001, Zhang *et al.* 2013), crocin (Chen *et al.* 2004), phenylethanoid glycosides (Ouyang *et al.* 2003), alkaloids, raubasine, and flavonoids (Evans 1983, Yuan *et al.* 2002, Zhang *et al.* 2013) has been observed in *Taxus* sp., *Crocus sativus*, *Cistanche deserticola*, *Catharanthus roseus*, *Saussurea medusa*, *Tetrastigma hemsleyanum*, and *Ginkgo biloba*. The stimulation of secondary metabolite production may be associated with the stimulation of specific enzymes that control their biosyntheses (Yuan *et al.* 2002, Ouyang *et al.* 2003), and these enzymes respond to very low concentrations of REE (Evans 1983, Yuan *et al.* 2002). If Ce^{3+} and La^{3+} are added to the medium the cell growth is stimulated as well as the amount of specific metabolites (*e.g.* carotenoid crocin) and their effect on plant physiology can be synergic (Chen *et al.* 2004).

Growth and yield of crops and tree species

Negative, positive, or no effects of REE on plant growth, and crop and tree yields have been observed in many countries around the world since 1933 (Hu *et al.* 2004). Application of REE in a form of foliar spray, additions of solid or liquid fertilizers, and seed treatments were used in more than 100 species (Hu *et al.* 2004, Redling 2006).

Low concentrations of REE stimulate growth, whereas high doses of REE inhibit growth (Zeng *et al.* 2006, Emmanuel *et al.* 2010a,b, Zhang *et al.* 2013). The REE application can have a beneficial effect by improving the growth and development of plants when supplied in an appropriate concentration (Xu and Wang 2007, Zhang *et al.* 2013). However, an excess of REE can cause toxicity (Gonzalez *et al.* 2014), which depends on

the plant species and soil. Two indicators which might help to determinate a critical REE concentration are Chl *a/b* ratio and leaf POD activity (Zeng *et al.* 2006).

Impact of Ce on lichen *Xanthoria parietina* was also investigated. A decreased sample viability is a consequence of Ce (0.1 - 100 mM) toxicity. Moreover membrane lipids peroxidation, ultrastructural changes and decreased photosynthetic performance are recorded (Paoli *et al.* 2014).

There are two opposing opinions concerning REE toxicity: *a*) REE are of limited toxicity and not considered extremely hazardous to the environment (Thomas *et al.* 2014); *b*) a slow accumulation in the environment could become a problematic issue - the

situation in soil ecosystems is considered as becoming a serious environmental problem (Zhimang *et al.* 2001). The first opinion is also supported by Rühling and Tyler (2004), who demonstrated changes in the content of REE and other elements in moss carpets in south Sweden. Content of REE significantly and considerably decreased between 1975 and 2000. The median content of REE in soil was 2.5 - 2.8 times higher in 1975 than in 2000. A similar result was obtained by Markert and De Li (1991). Content of REE in forest species (*Betula alba*, *Pinus sylvestris*, *Vaccinium vitis-idea*, *Vaccinium myrtillus*, *Deschampsia flexuosa*, *Polytrichum* sp.) was in relatively narrow ranges between 1987 and 1990.

Nevertheless, possible ecotoxicological effects and mechanism of action of these elements are still poorly understood (Gonzalez *et al.* 2014). As shown in this review, there is no clear pattern of increasing or decreasing accumulation with atomic properties (Gonzalez *et al.* 2014), distribution, fractionation, or hyperaccumulation in different plants. However, there is no doubt that dramatic increases in REE content in soil ecosystems has become a serious problem in some cases (Zhimang *et al.* 2001). Because of many applications, their global production has increased exponentially in the last decades, and their natural biogeochemical cycles are being disrupted by human uses (Gonzalez *et al.* 2014). The results of experiments conducted on four citrus farms in Brazil are alarming. The total content of La, Ce, and Nd in orange juice was 4 to 5 times higher than safety levels of REE in drinking water (Turra *et al.* 2013). Further, high REE concentrations are inhibiting or are even toxic to plants grown around mining facilities (Anawar *et al.* 2012). The content of REE in mining areas might be even hundreds of times higher than in non-mining areas (Liang and Li 2014). Those REE are easily

mobile and are transported among different environmental components. They enter into food chains and may have harmful effects on human (Liang *et al.* 2014).

Information about the toxicological effects of REE on living organisms is very limited. Available studies have dealt rather with REE mixtures than with individual elements (Pagano *et al.* 2015, Rim 2016). In general, toxicity was observed mainly for soluble lanthanide compounds, such as chlorides, nitrates, and sulphates, whereas insoluble forms (carbonates, phosphates, and hydroxides) are practically non-toxic.

REEs behave similarly to other xenobiotics – they show stimulatory or protective effects at low concentrations but disruptive effects in high concentrations (Pagano *et al.* 2015). Broad extension of REE damage effects were recorded in humans exposed to rare earth elements dust: pneumoconiosis (Xiao *et al.* 1997), embolism, damage of liver (Palmer *et al.* 1987) or itching, sensitivity to heat and skin lesion (Pairon *et al.* 1995). It is supposed that REE can be metabolized in human body and some of them are probably biopersistent (Pairon *et al.* 1995).

As shown in the studies described above, the environment is changing as well as the REE content in it. One way to monitor the status of REE in the environment over the long-term is through biomonitoring. Biomonitoring can indicate REE contamination in soil and the atmosphere. Stand of *Juniperus communis* (Närhi *et al.* 2014), native plant vegetation (Durães *et al.* 2014), lichens (Anawar *et al.* 2012), carpet-forming mosses (Rühling and Tyler 2004, Tyler and Olsson 2006), and mangrove sediments (Silva-Filho *et al.* 2011) can serve as indicators of REE for evaluation of a possible anthropogenic impact.

Conclusions

The REE occur naturally in different ecosystems mostly depending on the rhizosphere (Fu *et al.* 2001). Nevertheless, near industrial and mining sites the concentration of REE can rise highly above common levels and become a part of soil and ground water. Especially some indigenous species (*Asclepias syriaca*, *Desmodium canadense*, and *Panicum virgatum*) – usually more sensitive than crops – can suffer from toxic REE concentration (Carpenter *et al.* 2015).

The effects of REE on plants can be divided into three groups: beneficial, inhibitory, and toxic (Redling 2006). However, the boundary between beneficial and inhibitory effects is very thin and depends on many factors resulting from the concentration and plant species. These factors include the origin of REE enrichment, soil, water content in soil and plants, the concentration of REE and their combination, redox potential, ability of elements to bind to compounds, and activity of soil bacteria, among others.

The most commonly described elements in the literature include La, Ce, Pr, Nd, Sm, and Eu, which are

widely used fertilizers (Hu *et al.* 2004). There are many studies describing the impact of REE on crops. More than 100 crop species have been shown to respond positively to REE, with yield increases of 5 to 15 % (Hu *et al.* 2004). The REE can affect many physiological processes in plants. The most commonly described effects include their effects on photosynthesis, Chl content, Rubisco activity, biomass production, cytoplasmic membranes, nutrient metabolism, hormone interactions, enzymes, water use efficiency, germination and growth, the amount of sugar and other metabolites, and the amount of vitamins, among others. Further, use of REE can improve plant resistance to diseases, e.g., the soft-rotten disease in cabbage (Hu *et al.* 2004).

There are further impacts of REE on plants than those described above, and some of the consequences are still unknown. However, it should be noted that the effect of REE on plants is comprehensive. We cannot exclude a positive effect on one species of plant and thus ignore negative consequences in a broader sense on the whole

ecosystem. Generally, REE at low concentrations promote growth, and high doses have inhibitory effects. However, there are large differences in the impact of REE on individual plants such as the distribution of elements within the plant, absorption of REE, fractionation, and influence of individual elements on specific parts of plants. Hyperaccumulators that have the ability to accumulate larger amounts of REE with minimal negative consequences to the plant itself, e.g., *Phytolacca americana*, are very interesting for a possible remediation (Wu *et al.* 2013).

An additional research could provide missing

information regarding the impact of REE on plant basic functions such as respiration or plant defense. The basic questions related to plant physiology were generally answered. Now the investigation should be focused on feedback of REE utilization in relation to animal and human health. It is known that REE can leach out into aquatic environments. It is absorbed by vegetation as part of the mineral nutrition and can enter the human food-chain (Chua 1998). Despite the research progress in the last few decades, certain areas of research are still missing, which could explain the inconsistent information regarding REE.

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