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Rare earth elements application in agriculture

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ABSTRACT

Rare earth elements (REEs) are a group of chemical elements that include lanthanides as well as scandium and yttrium. Today REEs are used in various industries, such as agriculture where they are used as micro fertilizers and feed additives, the latter being used in medicine as well. There is no indication that REEs might be essential for any form of life. At lower concentrations, they can favorably influence certain physiological processes of plants (enzyme activity, hormone content, photosynthesis, seed germination, plant growth, etc.). They may induce an increase in some antioxidant systems and thereby increase the tolerance of plants to environmental stressors caused by high concentrations of heavy metals, herbicides, lack of water and essential nutrients, UV radiation and oxidative stress. Thus, their favorable effect was documented regarding the yield of cultivated species as well as the effect of their chemical composition on the content of vitamin C, soluble sugars and essential elements, reduction of the concentration of toxic heavy metals, improvement of the quality of wheat kernel for different uses. REEs have been commonly used as feed additives in organic and inorganic forms in livestock production. The available literature on the use of REEs as feed additives in livestock suggests positive outcomes (affected various physiological processes, increase in milk, egg and meat production, promoted growth and reproductive performance), but further investigation and results are needed before extending their use to zootechnical purposes.

Keywords: rare earth elements, application in agriculture, yield, stress tolerance, feed additives

ИЗВОД

Групу елемената ретких земаља (ЕРЗ) чине лантаноиди (Ln) заједно са скандијумом (Sc) и итријумом (Y). Елементи ретких земеља имају шроку примену у бројним гранама индустрије и технологије. У пољопривреди се примењу као микро ђубрива и као додатак сточној храни. Према досадашњим сазнањима ЕРЗ нису биогени елементи за живе организме. Међутим, зависно од бројних чинилаца они могу да делују стимулативно, токсично или да њихово дејство изостаје на физиолошке и биохемијске процесе биљака (фотосинтезу, водни режим, минералну исхрану, клијање семена, толерантност према неповољним абиотичким чиниоцима, активност хормона и антиоксидантних ензима), а тиме и на растење и органску продукцију биљака. ЕРЗ утичу и на хемијски састав биљака на садржај витамина С, растворљивих шећера и минералних материја. Могу да смање коцентрацију токсичних тешких метала, побољшају квалитет зрна пшенице и др. Примењују се као појединачни елементи ЕРЗ или у виду њихове смеше, уношењем у зони корена, наношењем у виду раствора на надземне органе биљке и третирањем семена. Резултати истраживања у вези примене ЕРЗ у сточарству указују на њихово физиолошко дејство на активност хормона и ензима, антиоксидантни ефекат, активацију имуног система, искоришћавање и метаболизам хранива, антибактеријски ефекат, побољшање репродуктивних особина, повећање производње млека, јаја, меса и растења. Токсично дејство ЕРЗ код живих организама мање је проучавано и већином је фокусирано на La и Ce. Они се убрајају у мање токсичне елементе. Поред бројних резултата истраживања потребна су даља проучавања да би се ближе упознао мехнизам дејтсва ЕРЗ на животне процесе биљака и животиња, што би допринело њиховој широј и ефикаснијој примени у биљној и сточарској производњи.

Кључне речи: елементи ретких земаља, примена у пољопривреди, принос, отпорност на стрес, додатак сточној храни

1. Introduction

Rare earth elements (REEs) are present in small concentrations in all parts of the biosphere (Turra, 2017), but not in pure metal form. The average concentration of REEs in the Earth's crust ranges from 130 to 240 µg/kg, which is significantly higher than the concentration of some other micro elements. REEs comprise a group of heavy metals, often called lanthanides: 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). REEs, besides lanthanides, comprise also yttrium (Y) and scandium (Sc). Sc is associated with the REEs because of its position in the periodic table and its trivalent chemical affinity. Yttrium is frequently associated with REEs because of its small ionic radius (Aide, 2019). Sc and Y are considered REEs since they tend to occur in the same ore deposits as Ln and exhibit similar chemical properties (Balaram, 2019). Promethium, the rarest, occurs only in trace quantities in natural materials and most of its isotopes are radioactive with very short half-lives (Du and Graedel, 2013). REEs are very similar in chemical and physical properties. They have in some environments predominantly trivalent oxidation states, with the exception of Ce (also $^{4+}$) and Eu (also $^{2+}$). Lanthanides are considered as rare trace elements, which is not entirely true. Namely, the amount of Ce in the Earth's crust is slightly higher than the amount of Pb, Cu and Zn, and Lu and Tm than Cd and Se. Lanthanides are rarely found concentrated in one place. They are found in a wide range of minerals, including silicates, carbonates, oxides and phosphates (Balaram, 2019). There are over 250 minerals which contain REEs. Some important REE-bearing minerals associated with REE are: bastnaesite - $(La,Ce,Y)CO_3F$, monazite - $(Ce,La,Th)PO_4$, xenotime - YPO_4, pariite - $Ca(Ln)_2(CO_3)_3F_2$, loparite - $(Ce,Na,Ca)(Ti,Nb)O_3$, fergusonite – $REENbO_4$, and others (Dostal, 2017). Only bastnaesite, loparite and monazite are of economic importance. The total world reserves of REEs amount to 1326 t expressed in rare earth element oxides (REO). The largest part is found in China, 33.33%, then in Brazil and Vietnam, 16.67% each, and in Russia, 13.64% (US Geological Survey, 2018). It is estimated that world reserves of REEs will be sufficient for many centuries (McLeod and Krekeler 2017). Annual global consumption of rare-earth oxides is estimated at 150,000 t (Ganguli and Cook, 2018), and growth in consumption recorded between 2017 and 2021 is 13.7%. The dominant role in the production of REEs is played by China, which produces 78.7% of the world production of REEs. The US, Japan, and China are the three major consumers at the rare earth market. Recently, REEs have found application in numerous areas of human activity. The REEs, owing to their unique magnetic, phosphorescent and catalytic properties, are very important in the functioning of modern devices. Rare earths are critical components to many technologies that drive the modern world (Ganguli and Cook, 2018). Several elements of REEs are present in batteries that power every electric vehicle and hybrid - electric vehicle. They are also used in the production of laptops, lasers, digital cameras, mobile phones, solar panels, energy-efficient lighting, fiber-optics magnetic resonance tomography, wind turbines, polishing powders, glass additives, ceramics, fluid cracking catalysts, computers, medical technology, nuclear engineering, military devices and others (Kato et al., 2011, Kovariková et al., 2019). Rare earth oxides (REO) in the form of nanoparticles are widely used in polishing powders, catalysts, paint coatings and others. The REO might also enter the food chain, by entering in edible parts of the plants which is a potential threat to human health (Gui et al. 2017). REEs have found application in crop production and as feed additives in animal husbandry and in medicine (Balaram, 2019; Tommasi et al., 2021). Due to the wide application and the limited number of suppliers, REEs are considered critical raw materials in the European Union and beyond (European Commission, 2010). For the first time in the world, commercial REEs fertilizer was used in China. In 1980, 1330 ha of agricultural land was treated with RREs. Their application grew rapidly in the following period. In 1990, REEs fertilizers were used in agriculture in more than 20 Chinese provinces (Yu and Chen, 1995) on an area of 16-20 x 106 ha (Wu and Guo, 1995). Apart from China, in numerous other countries of the world, the impact of the application of REEs as micro fertilizers on the productivity and chemical properties of the products of cultivated species has been studied and their application has occurred (Hu et al., 2004; Wang et al., 2018).

2. Influence of REEs on growth, yield and chemical composition of plants

The effect of REEs on the growth and yield of plants depends on numerous factors, primarily on the type of element and its concentration, plant species, method of application, etc. Plants can take up REEs through roots and aerial organs. Water-soluble and exchangeable fractions of REEs are the most available. REEs are applied in a dissolved or solid state, by introducing them into the soil or nutrient substrate, by adding them to a nutrient solution, more often by applying them in the form of solution to the above-ground parts of the plant, by pre-sowing seed treatment, seed blending, or by immersing them in a solution of REEs. There is a large number of commercial fertilizers that contain REEs in nitrate, chloride and ammonium bicarbonate form and rare-earth complexes which contains amino-acids (Pang et al., 2002; Herraiz, 2015). There are also complex NPK fertilizers as well as liquid fertilizers with added REEs and macro and micro nutrients (Xiong et al., 2000; Backer and Solomon, 2020). REEs are still being used in phosphate fertilizers worldwide (Turra, 2017). Most often they are applied as individual elements, usually in nitrate and chloride form, and very rarely in the form of oxalate. As far as the individual REEs elements are concerned, studies are mostly focused on the effects of La and Ce (Tommasi et al., 2021). The amounts and concentrations of REEs in the treatment of plants depend primarily on the plant species, the stage of development and the method of application. Certain organs of plants also react differently to their application. In the case of treating above-ground parts of plants with a solution, the applied concentration of REEs ranges from 100 to 900, and most often around 400 mg/L. In the case of mixing (blending) seeds with REEs, 3 to 6 g of REEs/kg of seeds are mostly used, and when immersing seeds in a solution, 8 g of REEs/kg of seeds are applied (Guo, 1988; Pang et al., 2002). In the case of application in field conditions, 0.2 to 200 kg REEs/ha are applied by introducing into the soil. Positive effects at lower doses (<0.5 REEs/kg soil) are almost exclusively reported in Chinese literature (Thomas et al., 2014). When using individual REEs elements in the form of solutions, concentrations of 0.02 to 6 mg/L are indicated. In general, it can be said that the literature mentions very different concentrations and doses of REEs that have a beneficial or toxic effect on certain physiological and biochemical processes and thus on the growth and organic production of plants. Preference is given to the application of REEs by treating above-ground organs and seeds in relation to their introduction into the soil, since in there, depending on the chemical properties of the soil, they can change into forms inaccessible to plants.

3. Influence of REEs on life processes and plant growth

The paper of Chien and Ostenhout (1917), who studied the physiological effects of Ba, Sr and Ce in water-floss (Spirogyra), is cited as the first published paper regarding the study of the effect of REEs on plants. In the following period, numerous authors studied the effect of REEs and their individual elements on plants: Drobkov (1941) Ce, Sm and La, Evanova (1964) Ce, Horovitz (1965) Sc and others. Owing to the knowledge gained over time regarding the effect of REEs on plants, their commercial application in agriculture began in China in 1972, in the USA in 1979 (Guo et al., 1988), and in the UK in 1983 (Andrew, 1983). There are 92 elements present in the Earth's crust, out of which only 17 are essential for higher plants; 12 elements are considered to be beneficial in small concentrations, and among them the rare earth elements cerium and lanthanum (Pilon-Smits et al., 2009). Agathokleous et al. (2019) highlight REEs-associated hormesis i.e. stimulating effect of low and inhibitory (toxic) effect of high concentrations on the life processes of plants. According to Daumann (2019), beyond hormesis, REEs have been investigated as essential elements involved in important life processes, thus raising their biological significance to a number of different biota. Based on current knowledge, REEs are not essential elements for higher plants, since plants can normally complete their life cycle without their presence. In addition, depending on numerous factors, primarily on the applied concentration and dose, they can act as stimulators, as toxic, or have no effect on the life processes of the plant. A large number of scientific research and review papers regarding the influence of REEs on plants have been published in recent decades, which clearly indicates a growing interest in these micro elements (Hu et al., 2004; Kastori et al., 2010; Heneklaus et al., 2015; Ganguli and Cook, 2018; Aide, 2019; Belaram, 2019; Kovariková et al., 2019; Kotelnikova et al., 2021; Tommasi et al., 2021; Kastori et al., 2023). The effect of REEs on the growth, organic production and yield of plants stems from their influence on important physiological and biochemical processes of plants.

REEs affect photosynthesis. Their ultimate effect on photosynthesis, and other significant life processes of plants, primarily depends on the specific REE, applied concentration, method of application and plant species. It is believed that lower concentrations of REEs can have a favorable effect on the photosynthetic rate by chlorophyll formation, chloroplast development, increasing the light absorption efficiency, regulation of the excitation energy distribution of FS I and FS II, promoting activity of Hill reaction. In addition, REEs may stimulate carboxylation activity of rubisco and alleviate different kinds of stresses (Ma et al., 2017; Oliveira et al., 2018; Salgado et al., 2020, Ma et al., 2022). Beside photosynthesis, the water regime also plays a significant role in the growth and formation of plant yields. Depending on the applied concentration, REEs can have a stimulating or inhibitory effect on the growth of the roots responsible for water uptake (de Olivera et al., 2015; Ma et al., 2017; Kotelnikova et al., 2019; Salgado et al., 2020) as well as on the size and anatomical structure of the leaves, responsible for releasing water (Kastori et al., 1990; Maksimović et al., 2012; Maksimović et al., 2014). Lanthanum increases transpiration rate (Ma et al., 2017; Cui et al., 2019) and stomatal conductance (Zhou et al., 2011, Ma et al., 2017), leaf water potential and water content (Xu et al., 2007). Application of preparations containing La and Ce increased stomatal conductance and transpiration rate (Backer and Solomon, 2020), and the use of Ce increased water use efficiency in beans (Salgado et al., 2020). REEs also influence the uptake and thus the content of mineral substances in plants. It is believed that this is based on synergistic and antagonistic interactions of uptake between plant mineral nutrients and REEs. According to Lian et al. (2019) lanthanum nitrate improves phosphorus use efficiency under P-deficiencies in Vigna angularis. In rice, La increased the concentration of Zn, P, Mn, Fe, Cu and Ca in the root, decreased the concentrations of Mn, Mg, Fe and Ca in the straw and Fe and Ca in the grain but increased the concentrations of Cu in the grain (Xie et al., 2002). Based on the above, it can be concluded that La affects not only the uptake but also the transport and thus the distribution of elements in the plant. Some lanthanides (La^{3+}, Nd^{3+}) ions with an effective radius close to the Ca^{2+} ions might partially be able to replace endogenous Ca of plants or interact positively with Ca in various physiological functions. Lanthanum is also probably able to replace magnesium ions in chrorophyll $(Chl\text{-}a\text{-}La\text{-}pheophytin)^{2+}$. REEs can indirectly affect the supply of plants with nitrogen since they affect the activities of nitrogen-transforming soil bacteria. Nitrification in red soil increased by 20% at 0.15 mg La g^{-1} dry soil but decreased at higher rates of application (Zhu et al., 2002). The influence of REEs on plant productivity is partly explained by their influence on antioxidant enzyme activity (i.e. peroxidases and superoxidase dismutases) (Emmanuel et al., 2010), bearing in mind the adverse effect of reactive oxygen species (ROS) on plant life processes. REEs can also affect the hormone content in plants and thus their growth. According to Cui et al. (2019) content of hormones gibberellic acid and idolacetic acid are increased by $LaCl_3$ application in maize. In plants that are propagated by seeds, growth begins with their germination. The effects of RREs on seed germination and seedling growth are often contradictory depending on the applied dose, the method of their use and the REE. Stimulation as well as inhibition of seed germination is reported by Ramirez-Olvera et al. (2018), especially when higher concentrations are applied (d'Aquino et al., 2009). In addition to the favorable effect of low concentrations of REEs on plant growth, there are numerous research results that indicate the unfavorable impact of higher doses or concentrations (Table 1).

Table 1.
Influence of REEs on plant growth

Treatment	Plant species	Observed effects	Reference
0.09 mg La L^{-1} in nutrient solution	*Zea mays*	Increase in root growth by 36%	Diatloff et al. (1995)
0.05 to 0.75 mg La L^{-1} in nutrient solution	*Oriza sativa*	Increase in root volume and root weight	Xie et al. (2002)
0.50 to 0.25 mg La or Ce^{-1} L culture medium	*Triticum aesativum*	Inhibited primary root elongation, decreased dry weight of roots and shoots	Hu et al. (2002)
0.713 to 17.841 μM Ce / pot culture	*Pisum arvense*	Enhanced shoot and root growth	Shyam and Acry (2012)
10^{-5} to 10^{-3}μM Y in nutrient solution	*Zea mays*	Decreased shoot and root length and leaf area	Maksimović et al. (2014)
0.04 and 0.20 mmol Ce L^{-1} applied to the foliage, field exp.	*Cyclocarya poliurus*	Increase in the relative growth of seedlings height	Xie et al. (2015)
2.8 to 22.2 mg La L^{-1} nutrient solution culture	*Glycine max*	Activated proliferation of root tip cells which is most likely a hormetic effect	de Oliveira et al. (2015)
100 mg La L^{-1} applied to the foliage field experiment	*Pseudostellaria heterophylla*	Increased main root and root tubor length	Ma et al. (2014)
200 mg La and Ce mg kg^{-1} soil	*Allium cepa*	Decrease in root elongation and mitotic index, with increased mitotic aberrations	Kotelnikova et al. (2019)

The same concentration or dose and chemical form(s) of individual REE in different conditions and methods of application to the same plant can have different effects. High concentrations and doses of REEs adversely affect the physiological and biochemical processes of plants and thus their growth and productivity, including cytogenetic effects and organ-specific toxicity. Most extreme environmental conditions and higher concentrations of some REEs can cause oxidative stress in plants and animals (Pagano et al., 2015; Zicari et al., 2018), modifying antioxidative stress enzyme activities and macro molecule composition (Rico et al., 2013). The explaination of a negative effect of higher concentrations of lanthanides on the cell lies in their ability to increase ROS generation. REEs toxicity relates to the induction of cytogenetic effects on the decreased mitotic activity, mitotic index, with increased mitotic aberrations (Kotelnikova et al., 2019). An increase in the Ho concentration increases in the number of cells with chromosome aberrations (Qu et al., 2004). There are plant species called hyperaccumulators that are able to accumulate significant amounts of REEs in their tissues, without adverse consequences (Liu et al., 2022). They can be used for phytoremediation at REEs-contaminated soils.

4. The influence of REEs on the yield and its chemical composition

As mentioned in the introduction, China has a leading position in terms of production and consumption of REEs in the world; therefore, it is understandable that the largest number of data regarding their application in agriculture and related to the impact on the yield and chemical composition of cultivated plants originate from that country. China is the first country in the world where commercial REEs-fertilizers were used. Numerous scientific studies in the field of agriculture in China indicate, suggest, demonstrate the favourable effect of low concentrations of REEs on the growth and productivity of cultivated plant species (Tyler, 2004). Experimental data suggest that the application of REEs may increase the yield by 5% to 15%, depending on the plant species (Hu et al., 2004). The application of individual elements belonging to REEs in some cases manifests a similar effect as the application of their mixture; however, in some cases significant differences may appear. Phosphate fertilization and liming were considered to be significant sources of REEs (Silva et al., 2019). Their regular application leads to an increase in the concentration of REEs in the soil, which also depends on the effect of REEs application on plant yield. The concentration of REEs in soil ranges widely (30-700 mg/kg) depending on their presence in parental materials, soil texture, organic material content, pedogenic processes and anthropogenic activities, which also needs to be taken into account when applying them. According to Heneklaus et al. (2015) the maximum effect of application of lanthanide fertilizers is achieved when their concentration in the soil is below 10 mg/kg, whereas at 20 mg/kg their effect is absent.

Today, in order to improve plant nutrition, REEs are widely applied in China's agriculture. Their application in agriculture is constantly growing from 1330 ha in 1980 to 1.4 million ha in 1989 and 16-20 million ha in 1996. Scientific experiments regarding their application have been carried out since 1972 (Buckingham et al., 1999). Experiments were performed under field and laboratory conditions and in greenhouses, growing plants on nutrient solution, in the soil and on various substrates, on a variety of plant species. Numerous research results indicate that the effect of REEs on the growth and yield of plants is characterized by a hormesis effect (Agathokleous et al., 2018).

The application of 750 kg/ha rare earth phosphate fertilizer (containing 0.04 – 0.06% of REEs) compared to calcium superphosphate increased the yield of corn by 17.0%, rice by 10.5%, wheat by 24.3%, potatoes by 18.5%, cabbage by 16.3%, turnips by 6.5% and Chinese cabbage by 16.4% (Xiangsheng et al., 2006). In nutrient solution, La at a concentration of 0.05 – 0.75mg/L increased the mass of rice root dry matter, 0.05 – 6 mg/L increased the number of grains, whereas 0.05 – 1.5 mg/L promoted yields (Xie et al., 2002). In a field experiment, 100 mg/L $LaCl_3$ and $CeCl_3$ solution applied (sprayed) to the Chinese cabbage leaves increased dry matter accumulation (Ma et al., 2014). According to Backer and Solomon (2020), application of water-soluble liquid fertilizer (REAP) which, in addition to La and Ce, also contained some micro and macro nutrients and EDTA at concentrations of 500 and 1,000 ppm increased lettuce, pepper, tomato and cantaloupe yield. Using mixed rare earth fertilizer in field experiment which contains La, Ce, Nd and Pr increased yield of Chinese cabbage and rape (Ren et al., 2016). According to Ou et al. (2014), foliar spraying of 0.5-1.5/L La increased the yield. Dry weights of root tuber yield of Pseudostellaria hterophylla significantly increased (by 58.34% and 56.87%) by foliar treatments of $La(NO_3)_3$ concentration of 100 mg L^{-1}, respectively, compared to the control (Ma et al., 2017). In field trials, seed pre-treated by soaking with $LaCl_3$ (800 µmol L^{-1}) significantly improved grain yield of maize (Cui et al., 2019). The yield of horseradish grown in a greenhouse on sandy soils in the treatment of leaves with 20 µmol/L La (III) increased by 25%, and in the treatment with 50/µmol L^{-1} La (III) by 16% compared to the control (Yang et al., 2019). REEs affect the metabolism of plants and thus their chemical composition. Application of REEs fertilizers alters biosynthesis of crop secondary metabolites, and these changes are often important for consumers since they may improve marketability of the crop. The stimulation of secondary metabolite production may be associated with the stimulation of specific enzymes that control their biosynthesis. Vitamin C in the fruit of strawberry increased at low concentrations of La nitrate application but was reduced at higher application rate (Shan et al., 2017). According to Ren et al. (2016), in leafy vegetables, Chinese cabbage and rape, in soil conditions, the application of mixed rare earth fertilizer (La,Ce,Nd,Pr) increased the soluble sugar content, titratable acid content, sugar/acid ratio and in spring the vitamin C content. The concentration of nitrates decreased, which is also significant, since their higher concentration in humans and animals leads to the creation of methemoglobinemia, which results in severe disturbances in the supply of tissues with oxygen. According to Zhang et al. (2013), application of $La(NO)_3$ and $Eu(NO_3)_3$ increased nitrate reductase activity in *Eriobotrya japonica* (loquat). In field studies, spraying the foliage with different concentrations of cerium nitrate increased the concentration of secondary metabolites like triterpenoids, quercetin and kaempferol in *Cyclocarya paliurus* seedlings (Xie et al., 2015). Spraying with 0.5 – 1.5 mmol L^{-1} La^{3+} improved the quality of wheat kernel for different end uses (Ou et al., 2014). In field plot experiments, using La and Ce, there was an increase in the vitamin C and nitrate content in the spring Chinese cabbage, while there was a decrease in vitamin C and nitrate content in the autumn (Ma et al., 2014). Heavy metals in higher concentrations are very toxic, therefore their entry into the food chain can represent a significant health problem for consumers. According to Ren et al. (2016) after mixed REEs termants, the heavy metals (Pb, Cd, Ni, Cu and Zn) content in Chinese cabbage and rape leaves and stems decreased. Plants are an important source of minerals for humans and animals, therefore their composition is of great importance, and it can be altered by RREs. Lanthanum concentration of 500 µg L^{-1} increased the uptake of nitrogen and phosphorus in spinach (Hong et al., 2005). The seed treatments with different Ce concentrations did not affect the concentration of macro or micronutrients in the shoots of rice. However, in the roots, the high Ce concentration decreased the concentrations of Ca, Fe, Mn and Zn, while the Mg concentration increased (Ramirez-Olivera et al., 2018). The contents of Mg, Ca, Fe, Mo, Cu, Zn and Mo in the horseradish treated with 20 µmol/L La are increased by 23.9, 25.4, 49.2, 70.5, 10.3, 21.0 and 85.9% respectively, compared to the control (Yang et al. 2019). The application of REEs does not lead to their significant accumulation in the above-ground parts of plants and thus does not threaten the health safety of food. For REEs elements it can be generally said that their distribution in plant organs is as follows: root > leaf > stem > flower > fruit. At a dosage of less than 10 kg/ha of REEs, no accumulation of individual REEs were detected in aboveground biomass and grains in maize (Heneklaus et al., 2015). In several studies, a very low concentration of REEs was found in cereal grains even in the case of fertilization with REEs (Redling, 2006). The REEs content in the main organs of the orange decreased in the following order: root > leaf > peel > pulp (Cheng et al., 2015).

5. The influence of REEs on plant stress tolerance

During vegetation season, plants can be exposed to unfavourable abiotic factors, which adversely affects their growth and development. Stressful conditions caused by unfavourable abiotic factors lead to the creation of reactive oxygen species (oxidative stress). They are produced by reduction or activation of O_2 and they are very reactive and cytotoxic in all organisms. Reactive oxygen species (ROS) like hydrogen peroxide (H_2O_2), singlet oxygen ($^1O_2$), hydroxyl radical ($^{\bullet}OH$), superoxide anion ($O_2^{\bullet -}$) cause disturbances in the growth and development of plants, lead to damage of cellular components and peroxidation of membrane lipids. For example, cadmium toxicity causes oxidative damage due to overproduced $O_2^{\bullet -}$, H_2O_2 and MDA in rice (Wu et al., 2014) and aluminum-induced oxidative stress in maize (Boscolo et al., 2003). A negative effect of the REEs growth characteristics of plants are explained by its ability to influenced the formation of reactive oxigen species, thereby stimulating lipid peroxidation (Siddiqui et al., 2019). Reactive oxygen species become toxic when their level exceeds the detoxification capacity of plant tissue. Plants have nonenzymatic (carotenoids, flavonoids, tripeptide glutathione, plant phenols, vitamin C and E) and enzymatic antioxidants (superoxide dismutase, catalase, ascorbate peroxidase, glutathione-S-transferase, glutathione reductase) in their cells. Antioxidants can protect plants against ROS, which accumulate during stress. REEs were found to be able to improve the resistance of plants to ROS by induction of enzymatic antioxidant activities (peroxidase, catalase, superoxide dismutase) or reacting with ROS directly (Wang et al., 2009). According to Yan et al. (1999), under an acid rain, REEs can significantly reduce the sensitivity of antioxidant enzymes to acid stress in wheat.

Human activities often lead to the accumulation of heavy metals in the soil, they are phytotoxic in higher concentrations (Kastori et al., 2020) and lead to oxidative stress in the cells (Un-Haing and Nam-Ho, 2005). According to Pang et al. (2002), La increases antioxidant enzymes activity in wheat seedlings enhancing their tolerance to lead stress. Many herbicides used in agriculture cause oxidative stress. The tolerance of certain plant species to herbicides is based on their ability to synthesize various antioxidants that exert a protective effect in conditions of oxidative stress. Jia et al. (2005) reported that La promotes the activity of damages caused by pesticides (2,4-Dichlorophenoxy). According to Ippolito et al. (2011) La(NO_3) treatments induced an increase in some antioxidant systems and this stimulation does not improve the plant responses to the drought stress. High doses of non-ionizing UV-B radiation lead to membrane lipid peroxidation and protein oxidation, which is associated with ROS. Mao et al. (2012) reported protective effect of Ce ion against ultraviolet B radiation – induced water stress in soybean seedlings. Cerium could promote maize seedlings growth under potassium deficiency, salt stress and combined stress of potassium deficiency and salt stress, decreased oxidative stress and increased antioxidative capacity in leaves caused by different stresses (Hong et al., 2017). Salgado et al. (2020) reported Ce alleviates water stress in common bean plants. According to Zhou et al. (2011) cerium relieves the inhibition of chlorophyll biosynthesis of maize caused by magnesium deficiency.

6. REEs as feed additives in livestock

The use of REEs in animal husbandry as feed additives started in China several decades ago (Ji and Cui, 1988). Numerous research results obtained in the past indicate the biological effect of REEs when they are used as feed additives (Abdelnour et al., 2019, Tariq et al., 2020, Tommasi et al., 2021). It is believed that REEs excert a variety of effects, like impact on hormonal and enzyme activities, antioxidant effects, stimulation of proliferation of specific cells, activation of immune system, enhancement of digestibility and nutrient utilization, metabolism of nutrients, improve reproductive performance, increase of the plasma concentrations of Ca and P and have antibacterial effect. Chemical form and the concentration of REEs are observed to have a great impact on their efficiency as feed additives. Lanthanum and cerium in their citrate forms are available in the market as REEs feed additives, with recommended concentration range between 150 and 300 mg/kg feed (Abdelnour et al., 2019). According to He and Rambeck (2010) REE citrate or REE chloride at low doses of dietary (70 mg/kg) increased gain in body weight and feed conversion ratio of broiler chickens. Cerium oxide supplementation to laying hen diets increased egg production, feed conversion ratio and egg shelf life and significantly decreased superoxide dismutase and malondialdehyde concentration (Bölukbasi et al., 2016). Agbede et al. (2001) found that La2O3 (100-300 mg/kg) supplementation in broiler chicken increased total weight gain and altered heart, spleen and liver weights. According to Cai et al. (2018), REE-enriched yeast supplementation in finishing pigs increased linearly feed conversion rate, and average daily feed intake with increasing level of REE-enriched yeast in diet. Durmuş and Bölükbaşi (2015) reported that 200 mg/kg of lanthanum oxide in a diet of laying hens significantly increased shell breaking strength of eggs, whereas at 400 mg/kg diet it increased egg production and feed conversion rate.

Toxicological studies of REEs on human and animal health are relatively rare and mostly focused on the effects of La and Ce. Accumulation of REEs in the organisms of animals can result in: progressive pulmonary fibrosis and pneumoconiosis, necrosis in hepatic tissues, hyperactive lymphoid follicles, loss of motor function, epileptic fits and damages of nephrological system (Abdelnour et al., 2019). Additional toxicological studies are needed to gain a clear insight into the mechanism of toxic effects of REEs on animal health and productivity.

The available literature information for REEs use as feed additives may suggest beneficial effects of their application.

7. Conclusions

The rare earth elements (REEs) present a group of elements which includes 14 lanthanides, yttrium and lanthanum. They have nearly identical chemical and physical properties. They are usually trivalent, rarely tetravalent or divalent. In small concentrations REEs are widely present in nature. Global production and use of REEs in various industries have increased exponentially in recent decades. They are also used in agriculture, in plant production as micro fertilizers and as feed additives in livestock production. China has a dominant position in terms of production, consumption and application of REEs in agriculture. In plant production, they are applied in a solid or soluble state, by introducing them into the root zone, by pre-sowing seed treatment or by applying them in the form of a solution to the above-ground parts of the plant. They may be used in mixtures or as individual elements. Depending on the applied concentration, type of element, plant species, method of application and environmental conditions, REEs can favourably affect the life processes of plants and thus their growth, organic production and yield. Since REEs also affect the secondary metabolism of plants, they affect chemical composition of crops and thus the quality of agricultural products. Beneficial effect of REEs on the tolerance of plants to adverse abiotic factors (drought, heavy metal, salt, UV-B radiation, oxidative, water stress) was demonstrated on many occasions. Several studies have shown the ability of REEs as feed additives to enhance feed conservation rate, average daily feed intake, average daily weight gain and health status, antioxidant effects, milk and egg production. The toxic effect of REEs in living organisms is less studied and is mostly focused on La and Ce. REEs are generally identified as not very toxic but further research is needed before practical proposals can be drafted for zootechnical use.

REEs are not essential elements for living organisms. Their effects on life processes in plants and animals range from stimulation to inhibition, as a function of their concentration (hormesis), mode and time of application. Further studies are needed to better understand the mechanism of action of REEs on physiological and biochemical processes and thus their impact on the productivity of plants and animals.

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