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## RARE EARTH ELEMENTS — YTTRIUM AND HIGHER PLANTS\*

**ABSTRACT:** Rare earth elements (REEs) form a chemically uniform group with very similar physical and chemical properties. The REEs include the elements scandium, yttrium, and the lanthanides from lanthanum to lutetium. They are widely distributed and present in all parts of the biosphere. REEs are required in industry, agriculture, medicine, biotechnology, environmental problems and many other fields. Lately, many experiments show their positive or negative, first of all nonspecific, effect on life processes of higher plants as well as growth and yield of cultivated species, but the physiological mechanisms are still not well understood. It has been determined that yttrium is widely distributed in plants, as well as that certain plant species uptake yttrium at different extent. Its highest accumulation is in the root and the leaf. Although yttrium was discovered more than two centuries ago, its effect on higher plants — their anatomical and morphological built, physiological and biochemical processes etc. — is very little known. One of the basic reasons is that yttrium, as well as other REEs elements, according to current knowledge, is not biogenic for higher plants and — wider — for live organisms. The objective of this paper is to concisely show previous knowledge about yttrium in the plant world.

**KEY WORDS:** Rare earth elements, yttrium, soil, plant, uptake, content, distribution, functions

### INTRODUCTION

There are 94 elements in the nature that are more or less present in all parts of the biosphere, but not all of them are biogenic for live organisms. For higher plants, biogenic mineral macroelements are C, N, P, S, K, Ca, and Mg, microelements are Fe, Mn, Zn, Cu, B, Mo, Cl and Ni, and beneficial elements are Na, Si and Co (Marschner, 1995). Numerous papers report that in par-

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ticular conditions the elements that are not essential for higher plants can stimulate their growth and development too. Stimulating effects of low concentrations of titanium (Pais, 1983), lead (Diehl et al., 1983), fluorine (Hitchcock et al., 1971, Kastori and Petrović, 1983, 1984), chromium (Krstić et al., 1991) and other elements on the growth and development and physiological and biochemical processes of plants were established. Stimulating effects on plants have also been attributed to rare earth elements (REEs). The REEs form a chemically uniform group and include the lanthanides and actinides. Due to many similarities, lanthanides are often marked with the common symbol Ln. The term lanthanides strictly defined refers to 15 elements following lanthanum to lutetium in the periodic table: 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). Yttrium (Y) and scandium (Sc) are often included in the list of RREs (Tyler, 2004) and scandium (Sc) (Hu et al., 2004). The element Y, which lies above La, and has a similar +3 ion with a noble gas core, (Ar), has atomic and ionic radii close to those for Tb and Dy. It therefore resembles them closely in its chemistry and is generally found in nature with the lanthanides. The lanthanides plus Y are commonly called the rare earths, although many of them are relatively abundant (Cotton and Wilkinson, 1988). Numerous research of REEs also include yttrium, which makes it necessary to review the REEs effect when studying yttrium's effect on organic production and life processes of plants. Even more so, since numerous investigations by now showed REEs effect on physiological and biochemical processes, growth, development and yield of plants (Hu et al., 2004). Detailed review of REEs in biological systems and their implementation is given in works of Brown et al. (1990) and Horowitz (2000).

### *Physiological effects of rare earth elements on plants*

On average content of REEs on the Earth, crust is close to 0.015%. More than 250 kinds of minerals containing REEs are known, among which the best known are: bastnaesite, monazite, xenotime, loparite, euxenite, and parisite. Content of REEs in the soil depends among other things on characteristics of the basic substratum and descends according to the following sequence: granite > quaternary > basalt > purple sandstone > red sandstone. Besides, content of REEs in the surface layer of soil depends also on pedogenetic processes, weather, content of organic matter and clay minerals etc. According to Bohn et al. (1985), content of REEs in the soil is in the range 30—700 mg/kg. Anthropogenic sources of REEs are phosphoric mineral fertilizers, phosphorus plaster, sewer mud, and atmospheric deposition. Origin, content, and dynamics of REEs in the soil are comprehensively considered in works of Tyler (2004) and Hu et al. (2006).

Physiological aspects of REEs were mainly researched by Chinese researchers and the results were mostly published in Chinese language. Detailed

review of these and other researches in the field were given by Hu et al. (2004). Work of the mentioned author presented the basis of summarized knowledge on uptake and effect of the REEs on physiological processes in plants in this review.

Plants can uptake the REEs through the root as well as the aboveground organs. Intensity of uptake of REEs and single elements of this group depends on numerous factors. There have also been determined synergism and antagonism between certain elements of the REEs during uptake. Their mobility in plants also differs. It is considered that Casparian strip of the root limits the transport of the REEs in the root. Use of EDTA encourages uptake of REEs, since this organic ligand increases desorption of REEs in the soil (Yang et al., 1999). Degree of translocation of REEs from the soil into plants is about 20%. They are mostly accumulated in the root, and less in the stem and reproductive organs. They are found in both intracellular and extracellular parts of a plant and form chelate compounds with numerous components of metabolism — amino-acids, nucleic acids, proteins etc. Uptake of REEs through the leaf is much faster than through the root. This is not characteristic only for the REEs, since the ions of other elements have far more faster uptake through the leaf and are included in the metabolism of a plant than when the uptake goes through the root.

Tyler (2005) states increase of concentration of most of the 58 examined elements, among which also REEs, on dry mass basis during the course of beech leaf senescence. According to Tyler and Olsson (2005), no clear relationship between soil properties or REEs content and leaf REEs concentration was detected in eight forest-floor herbaceous plants.

REEs affect the uptake and metabolism of mineral matter in plants. They stimulate the uptake of certain elements, and decrease the uptake of others. Their influence on the uptake and function of calcium was studied the most (Brown et al., 1990). The REEs have very similar chemical properties and ion radius as calcium. They bond at the same places in organism and have a similar effect as calcium. This mainly refers to  $\text{La}^{3+}$ . By using La it is possible to alleviate symptoms of calcium deficiency and stimulate growth of plants showing deficiency of this element. Similarly to calcium, REEs influence the stability, permeability and functioning of cell membranes and can inhibit calcium uptake (Rengel, 1994).

Hu et al. (2004) state in their paper results of numerous authors who have determined effect of certain REEs on activity of some enzymes, the content of phytohormones, productivity and intensity of photosynthesis, chlorophyll synthesis, translocation of photosynthesis products, water regime of plants and their resistance to water deficiency, symbiotic fixation of atmospheric nitrogen etc. But also, a favorable effect of REEs on seed germination has been determined by a larger number of authors (Chen Shu-Linang et al., 1987, Bai Bao-Zhang et al., 1988).

Research results about the REEs effect on plant growth are somewhat contradictory. The early findings mostly point to inhibitory effect of these elements on plant growth, first of all lanthanum (Pickard, 1970, Van Stevenick et al., 1976). In most papers published lately it is pointed to a sti-

mulating effect of REEs on growth and organic productivity of plants. They were found to affect favorably the yield of many grown crops such as rice (Hung Zhi-Gang et al., 1983), sugar cane (Ning Ja-Ben et al., 1985), sugarbeet (Xie Hui-Guang and Yu Zheng-He, 1986, Bai Bao-Zahng and Wang Ting-Hui, 1988), soybean (Kastori et al., 1990b), sunflower (Bai Bao-Zhang et al., 1990a).

### *Yttrium in plants*

In 1974 Finnish chemist Johan Gadolin has investigated a mineral discovered by Arrhenius in 1787 in Sweden in the village of Ytterby, and obtained an oxide, which he named ytterbia. The product was a mixture of oxides from which in 1843 Mosander obtained yttrium-oxide, and later in 1928 Wöhler managed to obtain the metal yttrium (Greenwood and Earnshaw, 1999).

In nature yttrium can be found in small quantities in polymetal minerals that contain compounds of lanthanides, calcium, iron, uranium, titanium, zirconium etc. The Earth crust contains about  $5.0 \times 10^{-3}$  weight percent of Y. Sources of Y are ores xenotime, gadolinite, samarskite etc. Apollo missions to the Moon showed that there is a very high content of Y in moon rocks ([www.graysonhighschool.org](http://www.graysonhighschool.org)). In chemical compounds Y is found in the form of cation  $Y^{+3}$  or is a part of complex anions. Y salts are colourless, they hydrolyze, tend to form double and complex salts. It forms inorganic and chelate compounds and alkyl products (Ripán and Ceteanu, 1972).

Interest and demand for Y have suddenly increased since the production of colour TV screens began, for some of its compounds found use as material that glow under stroke of electrons (Ribár, 2006). Yttrium is also used to create fake games, lasers, radar equipment, camera lenses and so much more. Metal Y and its compounds and isotopes are lately used in different contemporary technologies and instrumentation, as well as medicine and biotechnology (Horovitz, 1995). Research on its impact on physiological and biochemical processes in plants are more recent, they began at the end of the last century and are still rather rare.

Content of Y in the soil depends on litogenic and pedogenic processes, chemical composition of the rocks and minerals, physical and chemical properties of the soil and anthropogenic factors. Ultramafic rocks contain somewhat smaller amounts of Y (0.5 to 5 ppm) than acid rocks and sandstones (28 to 55 ppm) (Kabata-Pendias, 2001). According to Erdaman et al. (1976) content of Y in non-cultivated soil in the Missouri area USA is 23 ppm, while in cultivated soil it is 15 ppm. Gough et al. (1988) has determined in different types of soil in Alaska content of Y of < 4 to 100 ppm (DW). Ichihashi et al. (1992) have reported that content of Y in the soil is in the range, have reported that content of Y in the soil is in the range < 10 to 150 mg/kg. Based on the results of numerous authors it can be concluded that the content of Y in the soil is about 20 ppm. In the soil, yttrium forms complexes with proteins and humus matter (Paulenova et al., 2000). The adsorption process of Y-90 in soil was influenced by the soil type and the horizon's depth.

Hydrogen ions did not have a significant influence on the adsorption of Y-90 (Solecki, 2004).

The man enriches the soil with Y with his activities, first of all by usage of mineral fertilizers. According to Kasinova et al. (1996) content of Y in nitrogen mineral fertilizers is the range 2–4 ppm. As said by Kádár (2000) in superphosphates of different year of make the content of Y was in the range 10.4–53.9 mg/kg, in potassium salt 0.07–1.12 mg/kg, while in the investigated nitrogen fertilizers it was present only in traces. Organic fertilizers also enrich the soil with Y. According to investigations by Yoshino and Goto (taken from Kabata-Pendias, 2001) the content of Y in the dry matter of rice straw was 0.061 ppm, while in the animal manure prepared from the same straw it was much higher, 0.73 ppm.

In nuclear fission reactions various isotopes of Y are produced in rather large amounts. Twenty six Y unstable isotopes have been characterized. Y-90 exists in equilibrium with its parent isotope Sr-90, which is a product of nuclear explosions. Because of this, the study of the uptake and accumulation of Y by plants is assumed important. As a result of the Chernobyl disaster in 1986, measurements of Sr-90 and Y-90 and other radionuclides were measured in Hungary. Levels in plants were 10–15 folds higher, respectively, than in the years 1981–1985 (Cseh and Kiss, 1993). The isotopes of Y are not apt to be as important as other fission products in the hazard evaluation of fission product absorption by plants. The uptake efficiency for Y varies from 2 to 4 orders of magnitude less than Sr, depending on the plant and nutrient environment (Rediske and Selders, 1953). According to Klechkovskiy and Tselishcheva (1957) plants absorb more radioactive strontium than yttrium, more yttrium than strontium is transported within plants.

First published papers about uptake of Y by plants originate from the beginning of the second half of the last century. At the time a large number of isotopes of different elements was obtained, of Y as well, which enabled their appliance in experimental work too. Spooner (1949) was one of the first to investigate the uptake of radioactive Y in plants. He established that the red and brown algae react differently in their uptake of Y and concluded that the uptake of Y by algae from sea water to be partly adsorption and partly ionic exchange with Y already associated with a cell. According to Nishita et al. (1961) the uptake of several radioactive fission products from contaminated soils by crop plants was different among plant species and conditions of growth. The relative order of magnitude of uptake of fission products by crop plants through the root system appeared to be:  $\text{Sr}^{89-90} > \text{J}^{131} > \text{Ba}^{140} > \text{Cs}^{137} > \text{Ru}^{106} > \text{Y}^{91} > \text{Pm}^{147} > \text{Zr}^{95} - \text{Nb}^{95}$ . Distribution of fission products in different part of investigated crop plants were: pea leaves 10.0, stems 1.55, pods 0.80, seeds 0.02, roots 385.0, bean leaves 6, stems 2, fruits 2, lettuce leaves 3, stems 1, radish leaves 5, roots 7, carrots leaves 4, roots 4 D.P.S./g. Accumulation of Y was highest in root and leaves of plants, but comparatively low in seeds, fruits, or edible roots. Jacobson and Overstreet (1948) established that dwarf pea plants accumulate Y in their leaves to only about 0.034 times the concentration in the soil. The mentioned fact points to the assumption that Y is strongly bonded in the soil, which makes its uptake and consequently

translocation to aboveground plant organs limited. This is supported also by the research results of Rediske and Selders (1954) which state that barley on sandy loam soil can accumulate only about 0.006 of the concentration of Y present in the soil (concentration in aerial tissues/concentration in soil). Some authors claim far larger concentration factor for REEs. Citing results of other authors, Hu et al. (2004) state that the natural translocation rates for REEs from soil to plant are approximately 20%, and for REEs fertilizer „Changle” this rate was 55—60%. According to Welch (1984) biological absorption coefficient (plant /soil ratio for the plant concentration of a given element plotted as a function of its concentration in the soil) for Y and other REE elements in terrestrial plants is 0.003. Dobrovolsky (1994) calculated higher value of 0.15.

The uptake and consequently accumulation of Y in plants is affected by numerous biotic and abiotic factors. Presence of chelating agents in calcereous soil encouraged the Y uptake in beans (Essington et al., 1963). The pH value of the environment also affects the Y uptake. According to Tyler and Olsson (2001) the concentration of all REEs, except Y, in the roots of the grass *Agrostis capillaris* was inversely and linearly related to the pH of the soil solution. The result of Rediske and Selders (1954) show that within the range of pH the uptake efficiency was proportional to the hydrogen ion concentration. The same authors established that the uptake into the aboveground parts of the bean plants and the amount of Y associated with the roots was proportional to the concentration of Y added to the nutrient solution. Earlier, Robinson (1943) established that entering gadolinite into the soil increases the uptake of REEs. According to Gu et al. (2000) in solution culture the uptake of Y increased. Ozaki et al. (2002) investigated the uptake mechanisms of Y and REEs for accumulators and non-accumulators species. Autumn fern (*Dryopteris erythrosora*) accumulator species showed no ionic-radius dependence of Y-REE uptake by leaves, while non-accumulator species showed an extremely high uptake for Y compared to REEs. Y-REE uptake by autumn fern was influenced by the addition of chelating reagents to the uptake solution, while no effect was observed for non-accumulators species.

The Y content in certain plant species was investigated by a larger number of authors. Based on the published results, it can be concluded that certain plant species accumulate this element at different extent. The Y content in plants was thoroughly investigated by Connor and Shacklette (1975) and Shacklette et al. (1978). These authors have determined in 10% of the investigated species a measurable concentration of Y. In edible plants the Y content is in the range 20—100 ppm (AW), the highest value was determined in cabbage. Cowgill (1989) investigated 71 plant species that belong to 29 families and established presence of Y in all of the 1100 analyzed samples. This big difference in distribution of Y in plants between results of certain authors most likely lies in different sensitivity of the applied determination methods and genetic specificity of the investigated species regarding Y accumulation. Based on what we know today, it can be said that Y is very abundant in the plant world. Compared to other plant species, ferns and lichens have a high content of Y (Ichihashi et al., 1992). That is confirmed

by Erämetsä and Ylioukanen (1971) who have established that Y concentration in mosses and bryophytes is in the range 2—200 ppm (DW). Far lower values for the same plants are stated by Bowen (1979) — for lichens from 0.2 to 2 ppm and for bryophytes from 1.3 to 7.5 ppm (DW). These results confirm that beside the genetic specificity of the species and probably the genotype, an important role in Y accumulation belongs to ecological factors, which may explain significant differences in Y content determined at the same species in different environments by certain authors. Duke (1970) has stated that the content of Y in food plants from tropical forest region goes from 0.01 to 3.5 ppm (DW). Relatively high concentrations of Y exist in species of the phylum *Mycophytophyta* (Horowitz, 1993). Comparing the stated values of Y content in plants to the values of some significant biogenic microelements (Mo, Co, Se, Ni etc.), it can be concluded that by commonness in plants they are very similar to yttrium.

Distribution of elements in plants depends on their mobility in the plant, physiological and biochemical role, morphological and anatomical properties, growth and development phase etc. According to Zhu and Chen the sequence of some REEs in plants is as follows:  $^{147}\text{Nd} > ^{141}\text{Ce} > ^{90}\text{Y} > ^{140}\text{La}$  (taken from Hu et al., 2004). Reiske and Sedlers (1954) point to poor translocation of Y from aerial tissues and translocation from the root. For REEs elements it can be generally said that their distribution in plant organs is as follows: root > leaf > stem > flower > fruit. According to Hong et al. (1999) Y is mostly accumulated in the root, than the leaf and the least in the stem. A significant accumulation of Y in the beans root was detected also by Rediske and Sedlers (1954). The mentioned authors believe that the large accumulation of Y in the root is not the result of the life activity of the root tissue, but firstly of its adsorption onto the surface of the root system.

Yttrium is not a biogenic element for higher plants, why it is understandable that there is very little data in literature on its affect on growth, development, and life processes of plants. The capacity of Y bonding to biomolecules is indicated by the formation of complexes with phosphorus-containing compounds, mucopolysaccharides and fluoride (Horowitz, 2000) and nucleic acids (Fujiwara et al., 1990). The first paper about the influence of Y on plant growth was published at the beginning of the century by Evans (1914). This author established that 1.7 mg  $\text{Y}^{3+}/\text{l}$  produced a diminution in cell division with irregular cell arrangements by hyacinth (*Hyacinthus* sp.) rootlets. Cytological studies of the effect of a 40 metal solution, among which 0.5 up to 5 mM of yttrium sulfate on root meristem of *Allium cepa* showed a common effect of colchicine type mitosis (Levan, 1945). According to tests performed by Young (1935) appliance of 500 mg  $\text{Y}^{3+}/\text{kg}$  sandy loam affected stimulating on the growth of grass timothy (*Phleum pratense*). Fänrich (1964) established that yttrium chlorides combined with boron either had no effect or showed a slight inhibitory effect. Appliance of solution of 50 mg/l of the single REEs La, Pr, Nd, Sm, Eu, Gd and Y as  $\text{RECl}_3$  on seeds, increased germination of wheat by 1.3 to 16.5% (Jie, taken from Hu et al., 2004).

Numerous data from literature point to a wide abundance of REEs (Hu et al., 2006) as well as to their physiological and biochemical effect on plants

(Hu et al., 2004). They are not biogenic for higher plants or for other live organisms, but can specifically influence their life processes. Experiments, performed mainly in China, show that the REEs can be beneficiary for organic plant production (Hu et al., 2004). Even with numerous results (Horowitz, 2000), it can still be said that it is not clear enough how they affect human and animal health, which makes it necessary to investigate further in this field, having in mind that by being applied in plant production they enter the food chain. There is far less data in the literature about the single affect of certain REEs elements on life processes of higher plants, which goes for Y too (Horowitz, 1993, 1995, 2000, Kabata-Pendias, 2001). Identifying the uptake, accumulation, distribution of REEs in certain plant species and therefore their entrance into the food chain, as well as their non-specific stimulating or toxic effect on plants, can be very significant ecologically too. Therefore, an increased interest of researchers lately for this group of microelements is understandable. What certainly contributed to this trend is the existence of new and much more sensitive determination methods.

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## ЕЛЕМЕНТИ РЕТКИХ ЗЕМАЉА — ИТРИЈУМ И ВИШЕ БИЉКЕ

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### Резиме

Елементи ретких земаља (REEs) су из хемијски униформних група са веома сличним физичким и хемијским особинама. REEs укључују елементе као што су: скандијум, итријум и лантаниде од лантана до лутецијума. Они су широко распрострањени и присутни у свим деловима биосфере. REEs се користе у индустрији, пољопривреди, медицини, биотехнологији, код проблема заштите животне средине и у многим другим пољима. У новије време, у многобројним огледима је утврђено њихово позитивно или негативно, пре свега неспецифично, дејство на животне процесе виших биљака као и на растење и принос гајених врста, али физиолошки механизми дејства још увек нису разјашњени. Утврђено је да је итријум широко распрострањен у биљном свету, као и да поједине биљне врсте итријум у различитој мери усвајају. Највеће је његово накупљање у корену и листовима. Иако је итријум откривен пре више од два века, о његовом дејству на више биљке, на њихову анатомску и морфолошку грађу, физиолошке и биохемијске процесе и др. веома мало је познато. Један од основних разлога за то је да итријум, као и остали елементи REEs према досадашњим сазнањима нису биогеми за више биљке и шире за живе организме. Циљ овог прегледа је да у сажетом облику прикаже досадашња сазнања у вези са итријумом у биљном свету.