RARE EARTH ELEMENTS AFFECTING THE BIOLOGICAL PROCESSES AND YIELDING ABILITIES OF CULTIVATED CROPS

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ABSTRACT. Rare earth elements affecting the biological processes and yielding abilities of cultivated crops. *The research work was conducted at the Estonian Research Institute of Agriculture in 1997–2002. For the trials a high-concentration original solution of rare earth elements (REE), resulting from the production process of AS Silmet, was used. REE solutions of different concentrations were used to treat the plants in several ways: soaking of seeds, application into soil with nitrogen fertilizer, added to tank-mixes in weed control in cereals, as diluted water solution for mixing into peat substratum, plants were sprayed with low-concentration solutions also during the growth period. Trials were conducted with the following crops: spring wheat, field and garden peas, lettuce, tomato and cucumber. In vessel trials the treatment of wheat prior to sowing with REE solutions of low till moderate concentration increased the mass of young plants depending on the concentration, duration of treatment and length of day by 5.9–26.2%. In field trials the yield of wheat increased by 14.0% under the influence of micro-amount of REE added to herbicide solution in weed control. Soaking of pea prior to sowing with REE solutions increased the mass of young plants and yield of row pods. Also the content of phosphorus and potassium in pea roots increased considerably. Thus, it can be concluded that REE affect even the uptake of plant nutrients.*
The best ways of use and optimum concentration of REE for field and greenhouse crops depend on the species, growth conditions and probably many other factors that would need further investigation.

Keywords: *rare earth metals, soaking, spraying, cereals, vegetables.*

Introduction

Rare earth elements, *i.e.* lanthanoids, are 15 chemical elements of the 6th period of the III group of the periodic system with the atomic numbers 57–71. Physical-chemical properties of all lanthanoids are very similar. Lanthanum, cerium, praseodymium, neodymium, promethium and samarium belong to the group of light earth metals. Rare earth elements are actually not so rare at all. Their group is on the 15th place among the more important components of the crust of the earth. Rare earth elements exist always together, *i.e.* in one and the same mineral, mostly as phosphates or silicates. Earlier the separation of rare earth elements from each other was due to their similarity very difficult and time consuming; today with the help of modern technology it has become much easier (Brown *et al*., 1990).

The biggest investigated resources of rare earth elements are situated, in decreasing ranking, in China, USA, India, on the territory of the former Soviet Union, in the Republic of South Africa, Australia, Canada; there are resources also in Scandinavia (Brown *et al*., 1990). Nowadays the production of rare earth elements has been concentrated to few big companies, which situate, as a rule, in the vicinity of deposits. AS Silmet in Sillamäe, which operates on the basis of imported raw material, is second in the world as to the production volume of rare earth elements.

First trials to investigate the effect of lanthanoids in plant production were performed in 1930ies. However, these studies were occasional and were performed mainly in fields other than agricultural sciences. A systemic study of agricultural use of rare earth elements was started in China in 1979. China, India, Australia and other countries of South-Eastern Asia, which possess the greatest resources of rare earth elements, are responsible for the majority of scientific researches in this field. The effect of lanthanoids on the physiological processes of plants, their toxicology and environmental hygiene, the technology of agricultural use, *etc*. have been investigated. It became evident that with the help of rare earth elements it was possible to affect the productivity and chemical composition of plants (Guo, 1985; Brown *et al*., 1990, Diatloff *et al*., 1995). In China, a special fertilizer has been developed, the main component of which is soluble compounds of rare earth elements, and a number of trials have been performed with it. The use of lanthanoids has increased yields by 6–20% depending on the crop, and improved even some of the quality indicators of the yield (Guo, 1985; Zhong *et al*., 1996). In recent years the use of fertilizers containing rare earth elements has increased in China at a high pace.

The professor of the University of Queensland, Colin Asher (1991) is of the opinion that although the Chinese agriculture uses rare earth elements on a vast scale and considers them to be effective, it is necessary to perform further experiments that are well controlled and documented in order to clarify the effects of these elements.

The effect of rare earth elements on cultivated plants has been studied only for a short time; there are yet many questions to be answered. Many studies reveal neither the methods nor the concentrations; they only mention the results. Different species have different sensitivity to rare earth elements and their concentrations; the results are considerably affected also by the application time (Guo, 1985; Bai *et al*., 1993, Shi *et al*., 1994; Diatloff *et al*., 1996).

When rare earth elements were started to be used as fertilizers, an interest was also taken to their possible toxicity. Corresponding studies have been performed in several countries. According to Thomas Haley, professor at the University of Arkansas for Medical Sciences (1985), the acute toxicity of lanthanoids is low. Even several other scientists assure that the use of fertilizers containing these elements is quite safe.

In Estonia, trials with solutions containing rare earth elements and nitrates were started in 1997 in cooperation between Valentin Suško, Doctor of Technical Sciences, Development Director of AS Silmet, and Malle Järvan, Doctor of Agricultural Sciences. Already the results of preliminary trials (Järvan, 1997) were interesting and served as basis for further studies. Within the framework of cooperation agreements between the Estonian Institute of Agriculture and AS Silmet in the years of 1997–2004 high-concentrated nitrate solutions of rare earth elements (REE) were tested on different cultivated plants both in the field and greenhouse conditions.

Materials and methods

For the trials a high-concentration solution of REE, resulting from the production process of AS Silmet, was used; the solutions contained 221–228 g REE oxides ($\sum R_2O_3$) per one litre. Of REE oxides La constituted 90.5%, Ce 4.0%, Pr 3.7%, Sm 0.1%.

In the conformity with trial variants the original solution was diluted with water to certain concentrations just prior to the establishment of trials. The control variant was water. REE solutions of different concentrations were used to treat the cultivated plants in several ways: soaking of seeds, application into soil together with nitrogen fertilizer, added to tank-mixes in weed control in cereals, as diluted water solution for mixing into peat substratum, plants were sprayed with low-concentration solutions also during the growth period. Trials were conducted with the following crops: spring wheat, field and garden peas, lettuce, tomato and cucumber.

For soaking of the seeds of spring wheat and pea, in the first stage of trials also provocatively high concentrations were used. Altogether 12 solutions with different concentrations were tested in which the content of $\sum R_2O_3$ varied from 220 to 0.05 g/l. Advancing from higher concentrations towards lower ones, it was tried to identify the most effective range of concentrations in order to perform trials with it in the future. Different soaking times were tested starting from 45 minutes to 24 hours, also different seasons (May-June and September-October), *i.e.* the effect of different day length was identified.

The majority of trials in which seeds were soaked in REE solutions were conducted in greenhouse conditions. Soaked peas were strained and pricked out into vessels onto moist peat substratum (pH_{KCl} 5.9, nutritive content moderate) and covered with sand. Wheat had 50 kernels per vessel, pea had 15 or 20 seeds; the necessary amount of seeds were counted ready before putting into solution. The trials had four replications. The sprouting of wheat and pea as well as the mass of plants, in some of the trials also the contents of N, P, K, Ca in the dry matter of plants were determined.

In 1999–2000 altogether 4 microplot trials were performed on mineral soil with garden pea that had been soaked in low-concentration REE solutions ($\sum R_2O_3$ 0.05; 0.1 and 0.2%) for 3.5 hours. The seeds of control variant were soaked in water. Pea pods were harvested according to their maturing, three times in each trial. The yield of raw pods was determined.

To study the effect of REE, which was applied to soil prior to sowing, on cereal, similar field trials were conducted in 2001 at the Olustvere Experimental Station of ERIA with the variety "Munk" and in Saku trial fields of Üksnurme with the variety "Tjalve". REE at the rates of $\sum R_2O_3$ 0.5 and 1.0 kg/ha were added to the Silmet's liquid nitrogen fertilizer, which contained 204 g/l N and 30 g/l Na and which was applied at the rate of N 60 kg/ha during pre-sowing tillage. The size of the trial plot was 45 m² in Olustvere and 35 m² in Saku. The trials had four replications. The yielding ability of wheat and the protein content of kernels were determined.

In 2001 and 2002, the effect of REE ($\sum R_2O_3$ 228 g/ha) added to herbicide solution was studied in field trials in Saku. As herbicide Granstar 10 g/ha + Starane 500 ml/ha were applied. The application rate of the spraying solution was 250 l/ha.

On greenhouse vegetables the effect of REE was tested in two ways. In trials with lettuce REE was applied in pre-diluted solutions to peat substratum before pricking out lettuce sprouts to it. Concentrations $\sum R_2O_3$ 1.08–108 mg per one litre substratum were tested. The yield per *vessel* and nitrate content of lettuce were determined.

During three years the effect of spraying the plants with REE solution on the yield and quality indicators, including taste, of greenhouse cucumber and tomato was investigated. The leaves of well-developed young plants grown in pots were sprayed a couple of days before planting them into greenhouse with solutions that contained 0.05 to 0.5% $\sum R_2O_3$. Plants of the control variant were sprayed with water. The trials had 5–6 replications. One plant made a replication, the yield was calculated per single plants. The taste of tomato was assessed two times, altogether by 29 people.

Trial results were processed variation-statistically by dispersion analysis.

Results and discussion

Soaking of the spring wheat "Satu" in REE solutions of different concentration was studied in five vessel trials (Järvan *et al*., 1999). The effect of REE on the tillering of wheat and the growth of young plants depended on the time of soaking and the concentration of solution.

A short soaking (45 minutes) in the solution of moderate concentration ($\sum R_2O_3$ 1.1, 2.2; 5.5 and 11 g/l) did not affect tillering. In the case of higher concentration tillering started to decrease slightly. As the result of a short-time soaking in REE solutions of moderate to high concentration ($\sum R_2O_3$ 1.1; 2.2; 5.5; 11; 22; 55;110 g/l), the average mass of wheat plants was 17.9–21.7% higher than that of plants soaked in water.

24-hour-long soaking in moderate concentration (($\sum R_2O_3$ 1.1–5.5 g/l) did not affect tillering, but increased the mass of young plants by 20.4-26.2%. Solutions with the concentration of >5.5 g/l $\sum R_2O_3$ were toxic to wheat – tillering was retarded and the mass of plants decreased considerably.

On the basis of the above two trial results it was decided that in the future it would be worth of continuing the trials with soaking wheat kernels in REE solutions of moderate till low concentration. Due to insufficiently described methods published in foreign (mostly Chinese) literature, it was unfortunately not possible to rely on the research of other scientists regarding the optimum concentrations of REE.

In the case of soaking wheat kernels in REE solutions of moderate till low concentration, the best effect on the growth of plants had the solutions the $\sum R_2O_3$ content of which was 0.1–0.5 g/l. At these concentrations the mass of young plants increased after 21-hour-soaking by 8.7–16.3% in trials performed in June and after 24-hour-soaking by 5.9–7.1% in trials performed in September-October. Probably the results of these two trials could be affected also by the difference in the length of day, which in June was on the average 18.5 hours and in the autumn trials 11.5 hours. In the season with less light (September-October) a short-time (12 hours) soaking of wheat kernels gave better results; in this case REE ($\sum R_2O_3$ 0.2–1 g/l) increased the plant mass by 13.3–16.9%

Seeds of the pea variety "Carneval" were soaked in REE solutions with the concentrations from moderate to high (Järvan, 2001). The concentration of 1.1 and 2.2 g/l $\sum R_2O_3$ had almost no effect on the sprouting of pea, but the higher concentrations reduced sprouting considerably. When the sprouting of pea that had been soaked in water was on average 93%, the concentrations >2.2 g/l $\sum R_2O_3$ reduced it to 78–56%. In the trials established in the beginning of May with the soaking time of 3.5 hours and at concentrations of 1.1–22 g/l, the average mass of pea plants increased by 13.0–27.0%. In the trials performed in the first half of June, a 4-hour-soaking at concentrations of 5.4–22 g/l $\sum R_2O_3$ increased the mass of pea plants by 21.8–31.0%. It was surprising that the treatment with solutions with very high concentrations (110 and 220 g/l $\sum R_2O_3$) resulted in a considerable increase in the mass of pea plants. Unlike in solutions with lower concentrations, in these solutions the peas did not swell, *i.e.* the solution of toxic concentration did not penetrate into seeds. Probably the positive effect of REE was due to the substance that remained on the surface of seeds.

While analysing the dry matter of pea's aboveground part and that of washed roots, it became evident that all concentrations of REE, except the maximum concentration 220 g/l $\sum R_2O_3$, increased the calcium content in the aboveground parts and reduced it in roots. The concentrations that were effective from the point of view of the growth of pea plants (5.5–22 g/L $\sum R_2O_3$), increased the phosphorus content in roots by 7.5–25.3% and that of potassium by 14.4–28.9%. Thus, it can be concluded that with the help of REE it is possible to influence the uptake of other nutrients. Several scientists (Leonard *et al*., 1975; Guo, 1985; Zhu *et al*., 1994; Diatloff *et al*., 1996) have identified in their trials with different crops that certain concentrations of REE have a positive effect on the uptake of phosphorus and potassium by roots and the movement of them to leaves; higher concentrations, however, inhibit the uptake of plant nutrients, the growth of roots and aboveground parts and may cause damage to leaves.

Soaking of the garden pea "Kelvedon Wonder" in low-concentration REE solutions for 3.5 hours before sowing increased the yield of raw pods in all four trials (Table 1). The effect of solutions with concentrations 0.05; 0.1 and 0.2% $\sum R_2O_3$ was almost similar; the yields increased about 20%.

Table 1. Effect of rare earths (ΣR_2O_3) on yield of garden pea

Concentration of soaking solution	Weight of pods, g/m^2				Average	
	I	II	III	IV	g/m^2	%
0	1406	1414	1233	1516	1392	100
0,05% ΣR_2O_3	1590	1722	1786	1610	1677	120.5
0,10% ΣR_2O_3	1547	1627	1863	1570	1652	118.7
0,20% ΣR_2O_3	1920	1861	1294	1709	1696	121.8
LSD 95%					235	16.9

The effect of REE applied before sowing to the soil on the spring wheat was studied in similar extensive field trials in Saku and Olustvere. REE, which was added to liquid nitrogen fertilizer and applied during tillage, resulted in Olustvere in an extra-yield of 149–310 kg/ha (Tabel 2). In the trial conditions in Saku, REE had no positive effect on the yielding ability of spring wheat. Neither did REE increase the protein content of kernels in the trials.

Table 2. Effect of liquid nitrogen fertilizer and rare earths on yield of spring wheat

Treatment	Olustvere, variety 'Munk'		Saku, variety 'Tjalve'	
	kg/ha	%	kg/ha	%
Without fertilizer	3570	100	4073	100
Liquid fertilizer N60 kg/ha	4587	128.5	4888	120.0
Liquid fertilizer N60 kg/ha + rare earths ΣR_2O_3 1,0 kg/ha	4897	137.2	4838	118.8
Liquid fertilizer N60 kg/ha + rare earths ΣR_2O_3 0,5 kg/ha	4736	132.7	4837	118.8
LSD 95%	275	7.7	388	9.5

Fertilization with REE is economically more efficient when performed together with some other agrotechnical method. It is possible that in certain cases there is also an effect of synergism. *E.g.* the treatment with REE and growth regulator together in the stage of shooting resulted in a bigger wheat yield than in the case of separate spraying (Zhang, 1985). In Saku the effect of REE, which was added to herbicide solution, on the yielding ability of cereals was studied during two years. REE at the application rate of $\sum R_2O_3$ 228 g/ha increased the yield of spring wheat "Tjalve" by 632 kg/ha, *i.e.* 14% (Järvan *et al.*, 2002).

Positive results regarding the treatment of spring wheat can be found even in the literature. Seed treatment and spraying with REE during the growth has increased the kernel yield in vessel trials by 5.2–14.0%, depending on the soil (Xie, Chang, 1985). In the field trials carried out by the same scientist in different parts of China, in which the seed was treated and plants sprayed with REE solutions, the yield of spring wheat increased on the average of four years by 11%. The yield increase was due to a bigger number of kernels in the head and a bigger 1000-kernel mass. The increase in the above yield indicators as well as in the number of productive shoots due to REE has been observed also by other researchers (Shi *et al.*, 1994).

At the Estonian Research Institute of Agriculture, the effect of REE on greenhouse vegetables has been studied too. In several trials with the lettuce "Cheshunt" REE was applied to peat substrata with pre-diluted solutions at different rates. The effect on lettuce yield and nitrate content was identified. It became evident that for lettuce the optimum REE concentration is between 10 and 50 mg $\sum R_2O_3$ per litre growth substratum (Järvan, 2001b).

Another possibility of using REE is the spraying of leaves with solutions of low concentration. At the ERIA such trials were started with greenhouse cucumber and tomato in 1998. Cucumber plants were sprayed at the stage of four true leaves, tomato plants directly before the emergence of the first inflorescence. Control plants were sprayed with water. A couple of days after the treatment the pot plants were planted into peat substratum. At first a wider range of REE concentrations were tested. A REE solution with the concentration of 0.5% $\sum R_2O_3$ caused leaf damages on cucumber and tomato plants, even necrotic spots, therefore the growth of sprayed leaves was retarded. New leaves developed normally. In further trials it was decided to use lower concentrations for spraying: 0.05, 0.1 and 0.2% $\sum R_2O_3$.

The cucumber F_1 "Strema" was affected positively by the spraying of young plants with the concentration of 0.1% $\sum R_2O_3$. It increased the average number of fruits per plant by 5.8 and the yield per plant by 0.67 kg, *i.e.* 11.2% (Järvan, 2001b).

In the trial with the tomato "Moneymaker" in 1999, the spraying of young plants with 0.1% and 0.2% REE solutions increased the yields by 11.7 and 10.3% (Table 3). The plants of these variants developed also more fruits. No pattern was found regarding the effect of REE on the biochemical composition of tomato fruits – the contents of nitrate, sugars and organic acids. However, the spraying of young plants with the concentration of 0.05% $\sum R_2O_3$ affected the taste of fruits. In the trial conditions of 2000, the concentrations of 0.05–0.2% $\sum R_2O_3$ did not increase the tomato yields.

Table 3. Effect of rare earths (ΣR_2O_3) on tomato

Concentration of spraying	Yield per plant, kg	Fruits per plant	Sugar %	Organic acids %	Taste
0	4.77	63.2	2.96	0.46	3.22
0,05% ΣR_2O_3	4.73	72.4	2.80	0.48	3.96
0,10% ΣR_2O_3	5.33	79.2	3.10	0.40	3.40
0,20% ΣR_2O_3	5.26	79.0	2.78	0.49	3.54
LSD 95%	0.51	13.3			0.47

Summary and conclusions

As the result of trials performed at the Estonian Research Institute of Agriculture in 1997–2002, it became evident that the use of rare earth elements, *i.e.* lanthanoids, makes it possible to influence the biological processes and yielding ability of field and greenhouse crops. REE solutions of different concentrations can be used in several ways: soaking or treating of seeds before sowing, application into soil or growth substrata, spraying of plants during growth, or as a supplement to tank-mixes in weed control or leaf fertilization. The best ways of use and optimum concentrations for field and greenhouse crops depend on the species, growth conditions and probably many other factors that would need further investigation.

The treatment of spring wheat prior to sowing with REE solutions of low till moderate concentration increased the mass of young plants in vessel trials depending on the concentration, duration of treatment and length of day by 5.9–26.2%. Solutions with the concentration of >5.4 g/l $\sum R_2O_3$ were toxic – tillering was inhibited and the mass of plants decreased considerably.

In field trials the yield of spring wheat increased by 14.0% under the influence of micro-amount of REE added to the herbicide solution in weed control.

Soaking of field pea prior to sowing with the concentrations of 5.5–22 g/l $\sum R_2O_3$ gave better results. Compared with soaking in water the mass of young plants increased by 21.8–31.0%. Also the content of phosphorus and potassium in pea roots increased considerably. Thus, it can be concluded that rare earth elements affect even the uptake of plant nutrients.

Soaking of garden pea prior to sowing with the low concentration solutions of REE increased the yield of raw pods on the average of four micro-field trials by 18.7–21.8%.

In the trials with greenhouse crops the spraying of leaves of young plants with low concentration solutions of REE had a positive effect on the formation of fruits and increased the yield of cucumber by 11.2% and that of tomato by 10.3–11.7%. However, the results were positive not in every trial with cucumber and tomato and not in every year.

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