Bioavailability and toxicity of bromine and neodymium for plants grown in soil and water

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Abstract Information about biological significance and possible phytotoxicity of many trace elements is still scarce. Bromine and neodymium are among the poorly investigated trace elements. In the research, greenhouse experiment was conducted to study effects of bromide of neodymium on wheat seedlings grown in soil and water. The wheat seedlings were capable of accumulating large amounts of both Br and Nd. Compared to the soil-grown plants, the water-grown plants accumulated higher concentrations of the trace elements. The bioaccumulation of Br and Nd resulted in statistically significant variations in the concentrations of several elements. The concentrations of P, Cl, and Ca in roots and Cl in leaves of the plants grown in the contaminated water and the concentration of I in roots of the soil-grown plants decreased. In the water-grown seedlings, the concentrations of Na and P were higher and concentrations of Mg and K were lower than those in the seedlings grown in soil. In leaves of the plants grown in water, the concentration of Cl was lower than in leaves of the soil-grown plants. In roots of the water-grown plants the concentration of Zn was higher and in leaves it was lower compare with Zn content in roots and leaves of the plants grown in soil. The K/Na ratios were 4 (leaves) and 20 (roots) times higher in the soil-grown plants, while, the Ca/Mg ratios were 8 – 19 times higher in the water-grown plants. Marked distinctions were also observed in relationships between different elements in the soil-grown and water-grown plants.

Key words Wheat; Bromine; Neodymium; Phytoextration from soil and water

Introduction

Information about environmental chemistry of many trace elements is still scarce and often contradictory. So far, only a very short list of so-called heavy metals has attracted much attention of researchers. Many other potentially toxic and/or biologically essential chemical elements often remain outside the major focus of scientists. Among these not well studied trace elements are bromine (Br) and neodymium (Nd). The role of Br and especially Nd in plant development and mineral nutrition is still poorly understood. Previously insufficient quality of analytical techniques used for determination of the elements in the environmental samples has been one of the chief causes of such a situation.

By 1999, the number of known natural organobromine compounds was over 1600 (Gribbe 1999). Later, the number of these compounds slightly increased (Gribbe 2015). Most of the bromides have been found in marine organisms. This is due to rather high concentration of Br in the sea and because this trace element can more easily be accumulated in plants growing in water. Terrestrial plants contain much less of such compounds.

The reported range of Br concentrations in plants growing in non-contaminated by bromides soils varies from <1 mg kg^{-1} to 30 mg kg^{-1} (Tensho 1970; Låg and Steinnes 1977; Gan et al. 1998; Wishkerman 2006; Sahin et al. 2012; Pourimani et al. 2013; Kabata-Pendias and Szteke 2015; Shtangeeva et al. 2017). Previously methyl bromide was the most well-known Br compound. It was used as a fumigant to regulate the soil-borne pesticides (Schneider et al. 2003). Although methyl bromide demonstrated a good effectiveness, it was found that the active use of the fumigant leads to depletion of the ozone layer (Shorter et al. 1995). Owing to this, the use of methyl bromide was limited in many countries. However, at present, numerous man-made Br compounds are widely used and released into the environment. Since these compounds may be toxic, it is important to study distribution of different bromides in soils and plants and estimate the fate of the Br bioaccumulation. Unfortunately, up to now, there is not enough available information on concentrations of Br in different plant species.

Among other lanthanides, there is much less information on Nd in the environment. This trace element is one of the most critical rare earth elements until 2025 (Freitas et al. 2020). One of the main applications of Nd is Nd-Fe-B magnets that are widely used in computers, cell phones and many other components (München and Veit 2017). The biological role of Nd is currently unknown. It is assumed that Nd is moderately toxic trace element (Zhao et al. 2019). However, it is possible that in the long run the accumulation of Nd in the environment may have severe effects.

According to available reports, the range of the Nd concentration in non-contaminated soils is 5.8-53 mg kg^{-1} (Tyler and Olsson 2002; Masto et al. 2011; Carpenter et al. 2015; Patra et al. 2020; Turra et al. 2020; Wang et al. 2020). In terrestrial plants growing in non-contaminated soils, the concentration of Nd can vary from 0.10 mg kg^{-1} to 2.0 mg kg^{-1} (Tyler 2004; Carpenter et al. 2015; Romero-Freire et al. 2019; Gorena et al. 2020). Although possible phytotoxicity of Nd is still poorly understood, it may be assumed that the toxic effects will depend on the concentration of the trace element in growth medium. It has been reported that at low doses Nd can have a stimulatory effect on the plant development (Luo et al. 2008; Rezaee et al. 2018) and reduce toxicity of well-known toxicants such as Cr (Lu et al. 2020).

The accumulation of elements in soil-grown plants is influenced by many different factors. This can make further interpretation of experimental results difficult. The process of uptake of elements by plants growing in water media is simpler. Due to this, until now, most of the experiments on phytoextraction of macro- and trace elements are usually carried out hydroponically. Meanwhile, it can be expected that the mechanisms controlling transfer of elements from growth medium to plants can differ when the plants grow in different media. In water, mineral elements are present in more available to a plant form and can be easily taken by roots. In soil, a certain part of an element is often adsorbed onto surface of the soil particles. Therefore, even though concentration of the element in the soil and water is the same, the roots will take from the growth media different amounts of the element. It may be assumed that translocation of elements from roots to upper plant parts will also differ in the water-grown and soil-grown plants.

Based on these assumptions, we studied effects of bromide of Nd on the plants grown under different conditions – in soil and in water. We performed the experiment when plants grow in non-contaminated soil and water and in the media contaminated by bromide of Nd. The research was addressed to a deeper understanding the Br and Nd pathways in plants and evaluation of the factors important for bioaccumulation of the trace elements. The main aims of the experiment were the following:

1. to study the potential of wheat to phytoextract Br and Nd from different growth media (soil and water);
2. to assess the effects of the Br and Nd bioaccumulation on the concentrations of other elements in the plants;
3. to examine the uptake of macro- and trace elements and to compare the relationships between the elements in the plants grown in soil and in water.

Materials and Methods

Experimental design

Eighty seeds of wheat *Triticum aestivum* L. were rinsed several times by ultra-pure water and germinated on a moist filter paper during five days. The five-day-old germinated seedlings were divided into two parts. One part of the seedlings was transferred to pots volume of 5 kg filled with soil. The soil had a loamy sand texture (74% sand, 24% silt, 2% clay). Second part of the seedlings was placed into vessels volume of 600 mL filled with tap water. Each series of the experiment consisted of two parts: one half of the seedlings were grown in non-contaminated media and second part was grown in the water or in the soil spiked with bromide of Nd ($NdBr_3 \times 6H_2O$). The concentration of Br in the solution was 50 mg L^{-1}. The wheat seedlings were grown in a naturally illuminated greenhouse during 10 days. A completely randomized design was used. The pots were watered daily. The air temperature was usually 25°C during the day and 22°C at night. The experiment was performed in triplicate. After sampling, the plants were carefully washed by deionized water and air-dried up to constant weight.

Elemental analysis

The extraction procedure used in the research was optimized in our earlier studies (Shtangeeva et al. 2015; Shtangeeva et al. 2017). In this procedure, the dried roots and leaves of wheat seedlings and reference material were weighed into the 50 ml conical centrifuge tubes (Falcon). Two ml of tetramethyl ammonium hydroxide (TMAH) solution were added to the vessels. Then the vessels were closed, and samples were heated during 16 hours in a sand bath at 60 °C. After extraction, the samples were diluted to 25 ml with ultrapure water. Before elemental analysis, the samples were stored in a refrigerator at a temperature of +5 °C. The ICP-OES (Agilent 5110 VDV) was used for determination of Na, Mg, P, K, Zn, and Mn. The concentrations of Cl, Br, I, and Nd were determined by ICP-MS. For the ICP-OES determination, all the samples were diluted to 1:2 with 5% (v/v) HNO_3; for the ICP-MS analysis, the samples were diluted 1:2 with ultrapure water. Neodymium (^{146}Nd) was measured by Agilent 8900 ICP-MS/MS. Furthermore, a Thermo Elemental X7 quadrupole

ICP-MS was used in the determination of ^{37}Cl, ^{81}Br and ^{127}I (Shtangeeva et al. 2015). The ion lens settings, nebulizer gas flow rate and torch position of the instrument were optimized to obtain the maximum ^{115}In count rate. To avoid matrix effects in sample introduction, halogens were measured from alkaline solutions (4% (v/v) TMAH). In addition, 4% TMAH (v/v) solution was used as a washing solution between the samples when halogens were measured.

Quality Control

For control of the quality of the analytical measurements was used standard reference material (SRM) Tomato leaves 1573a (National Institute of Standards and Technology, USA). The differences between the certified and informative values and concentrations of elements determined in the SRM in our work did not exceed 5-10%.

Data analysis

The multivariate statistical analysis of experimental results was carried out using Statistica for Windows 6.0 Software packages (StatSoft, Tulsa, OK, USA). Before analysis, the normality of the distribution of the analytical data was checked by the Shapiro-Wilk test. We calculated mean concentrations of elements and performed analysis of variances in order to assess statistically significant ($P<0.05$) differences between samples. Pearson correlation analysis and cluster analysis were used to assist in the identifying the factors that could influence on the bioaccumulation of elements and on the interactions between the elements in plants. This information can help in a better understanding the mechanisms that affect the uptake of elements and assess the relationships between elements that are typical for the plants growing in different media, including when the growth media are non-contaminated or contaminated by bromide of Nd.

Results and discussion

Bromine and Nd accumulation in wheat seedlings grown in soil and water spiked with bromide of Nd

As a result of growth of wheat seedlings in the soil and water contaminated by $NdBr_3 \times 6H_2O$ the concentration of Br in the plants increased (Table 1). The changes in the Br concentrations were different for the plants grown in water and soil. The concentrations of Br in roots and leaves of the water-grown plants increased much more than in roots and leaves of the plants grown in soil. The transfer of Br from roots to leaves also differed. In leaves of the water-grown wheat seedlings, the Br concentration was almost 2 times lower than in roots. In the soil-grown plants, the Br concentration in leaves was 1.5 times higher as compared to the Br content in roots.

Compared to control, the concentration of Nd in the wheat seedlings grown in the contaminated media increased significantly. A greater increase was observed in the plants grown in water medium. Roots accumulated more Nd as compared to leaves. The higher accumulation of Br and Nd in roots and leaves of the water-grown plants can be due to a better availability of nutrients and also non-essential trace elements to the plants grown in water media. It was reported that usually a large part of trace elements can be adsorbed onto roots, and only a small part of the elements will be transferred to upper plant parts (Chandra et al. 2009; Klink et al. 2013). Based on this assumption, we could expect lower Br and Nd concentrations in leaves as compared to concentrations of the elements in roots (when the plants grow in the medium enriched with bromide of Nd). In fact, this was observed for Nd, but in the case of Br, it was only found in the water-grown plants. When the wheat seedlings were grown in the Br-contaminated soil, the translocation of Br from roots to leaves was enhanced. In our previous experiment (Shtangeeva et al. 2017) we studied accumulation of Br in pea and wheat seedlings grown in the soils spiked with KBr and NaBr and also found that concentration of Br in leaves of wheat was always higher than in roots. On the other hand, transfer of this trace element from roots to leaves of pea was suppressed. Similar distribution of Br between roots and leaves of wheat seedlings was also observed by other researchers (Zhang et al. 2013; Zhu et al. 2020). One of the possible explanations for this phenomenon could be the following. Although the uptake of nutrients and trace elements by plants is affected by physical, chemical and biological soil characteristics (Chapin et al. 1987), the concentrations of elements in one or another plant species are determined by phylogeny of the plants (Watabene et al. 2007). That is why we often can observe quite different processes of element uptake and translocation from roots to upper plant parts in different plant species grown simultaneously and under the same conditions.

Variations in the concentrations of other elements in wheat seedlings resulting from bioaccumulation of Br and Nd

The growth of wheat seedlings in soil and water spiked with bromide of Nd also affected concentrations of some other elements in the plants. As expected, more serious effects were found in roots, especially in roots of the water-grown plants. Compared to control, the concentrations of P, Cl, and Ca in roots of the plants grown in the contaminated water decreased statistically significantly ($P<0.05$). In roots of the soil-grown plants such a decrease was found only for I. There were no statistically significant changes in the concentrations of elements in leaves of the soil-grown plants. In leaves of the plants grown in the water contaminated by $NdBr_3$ x $6H_2O$ we observed a statistically significant ($P<0.05$) variation only for Cl.

Thus, plants grown in water were more affected by $NdBr_3$ x $6H_2O$ contamination than plants grown in soil. It may be assumed that main effect on the decrease of halogens might be caused by bioaccumulation of Br (result of competition between chemically similar elements during their uptake by plants). An increase of Nd concentration in the seedlings could additionally lead to the decrease of P and Ca contents in the plants grown in the bromide contaminated water. The similar ionic radii of Nd and Ca suggest that Nd can compete with this essential plant nutrient. It was shown that Nd(III) can replace Ca(II) in plants (Wei et al. 2001; Zhang and Shan 2001). Rare earth phosphate is main component of rare earth ore (Onoda et al. 2002). Therefore, the relationship between Nd (rare earth element) and P is expectable.

Differences in the elemental composition of water-grown and soil-grown plants

Concentrations of almost all macro- and trace elements in the plants grown in soil and water differed significantly ($P<0.05$). In roots and leaves of the wheat seedlings grown in non-contaminated and contaminated water the concentrations of Na and P were higher and concentrations of Mg and K were lower than those in the seedlings grown in soil. Besides, in roots of the water-grown plants, the concentration of Zn was higher and in leaves it was lower in comparison with Zn content in roots and leaves of the plants grown in soil. In leaves of the plants grown in non-contaminated water, the concentration of Cl was lower and concentration of Br was higher as compared to concentrations of the elements in leaves of the soil-grown plants. In roots, the concentrations of both these elements were almost the same. In previous experiment, a higher accumulation of Br was also observed in leaves of the wheat grown in non-contaminated with Br liquid media (distilled water, spring water, nutrient solution of Hoagland) as compared to accumulation of Br in leaves of the wheat grown in soil (Shtangeeva 2017). One may speculate that the higher transfer of Br from roots to leaves of wheat is due to distinctive physiological characteristics of the plant species.

It is well-known that K and Mg play a vital part in plant development. Potassium is main inorganic cation in the cytoplasm of plants. This nutrient is essential for proper function of many enzymes (Marschner 1995). Magnesium is crucial in biosynthesis of chlorophyll and carbon fixation (Guo et al. 2015). The decrease in uptake of K and Mg implies that growth of plants in water may directly interfere with plant growth, development, and photosynthesis.

Ratios of essential nutrients in the plants grown in soil and water

Table 2 shows the ratios of essential nutrients in the plants grown in control and contaminated by bromide of Nd water and soil. The K/Na ratios were much higher in leaves and especially in roots of the soil-grown plants as compared with the K/Na ratios in the plants grown in water. On the other hand, the Ca/Mg ratios were higher in the water-grown plants than in the plants grown in soil. There was no effect of contamination of the growth media by bromide of Nd on the K/Na ratios in the plants grown both in soil and in water. In the soil-grown plants, the Ca/Mg ratios also did not change as a result of contamination of the growth medium. However, as compared to the wheat seedlings grown in clean water, the Ca/Mg ratios in the seedlings grown in the contaminated water were lower in roots and higher in leaves. As it was suggested, the toxic action of Nd on plants may include replacement of Ca/Mg (Sneller et al. 2000).

Statistical analysis of experimental data

Figure 1 shows results of cluster analysis of the wheat seedlings grown in non-contaminated and contaminated by $NdBr_3 \times 6H_2O$ media. Roots and leaves of the plants grown in soil were well separated into two groups (Fig. 1a). Moreover, in each group there was a good separation of the plants grown in clean soil and in the soil spiked with bromide. In the water-grown seedlings, the separation between roots and leaves, as well as between plants grown in non-contaminated and contaminated media, was less noticeable. (Fig. 1b).

The results of the correlation analysis clearly indicate the differences in the relationships between elements in the plants grown in the different media. In leaves of the soil-grown plants, the correlation between Mg and Ca – chemically similar elements – was statistically significant and positive ($r = 0.95$). In leaves of the plants grown in water, the correlation between these elements was also statistically significant but negative ($r = -0.82$). The correlation between concentrations of Ca in roots and leaves of the soil-grown plants was negative ($r = -0.83$, $P<0.05$). The statistically significant negative correlation was also found between concentrations of K in roots and leaves of the wheat seedlings grown in soil ($r = -0.71$). However, there was no correlation between concentrations of Ca (and also between concentrations of K) in roots and leaves of the water-grown plants. This fact can serve as additional evidence that mechanisms of accumulation of elements in the plants grown in soil and in water media are different. Therefore, there is reasonable to think that it is hardly possible to use experimental data on accumulation of different elements in the plants grown hydroponically in order to appreciate the mechanisms of the element uptake by the plants growing in natural conditions (in soil).

Conclusions

Our experimental results showed that growth of wheat seedlings in the media contaminated by bromide of Nd resulted in an increase of Br and Nd concentrations in the plants. The greatest accumulation was found in the water-grown plants. Compared to control, the concentrations of Br and Nd in the plant roots increased 215 and 340 times, respectively, while in the soil-grown wheat seedlings, the increase of Br and Nd plant concentrations was 10 times less. The bioaccumulation of these potentially toxic trace elements led to variations in the concentrations of several other elements. Plants grown in contaminated water medium showed statistically significant changes in the concentrations of P, Cl, and Ca (roots) and I (leaves). In the soil-grown plants, such a variation was observed only for I in roots. The concentrations of many elements (Na, Mg, P, K, Ca, and Zn) in roots and leaves of the water-grown plants differed significantly as compared to concentrations of the elements in the plants grown in soil.

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Compliance with Ethical Standards

The authors have no conflicts of interest to declare that are relevant to the content of this article. This article does not contain any studies involving animals or human participants performed by any of the authors.

Data Availability

The authors confirm that the data supporting the findings of this study are available within the article.

Contribution of authors to the manuscript

Study conception and design: Irina Shtangeeva; analysis of experimental samples: Matti Niemelä, Paavo Perämäki; draft manuscript preparation: Irina Shtangeeva. All authors reviewed the results and approved the final version of the manuscript.

Consent to Participate and Consent to Publish

Not applicable to the manuscript.

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Figure caption

Fig. 1 Cluster analysis (Ward’s method) of soil-grown (a) and water-grown (b) wheat seedlings.

l - leaves, r – roots of the seedlings grown in clean media (cont) and in the media spiked with bromide of Nd (Nd)

Figure 1

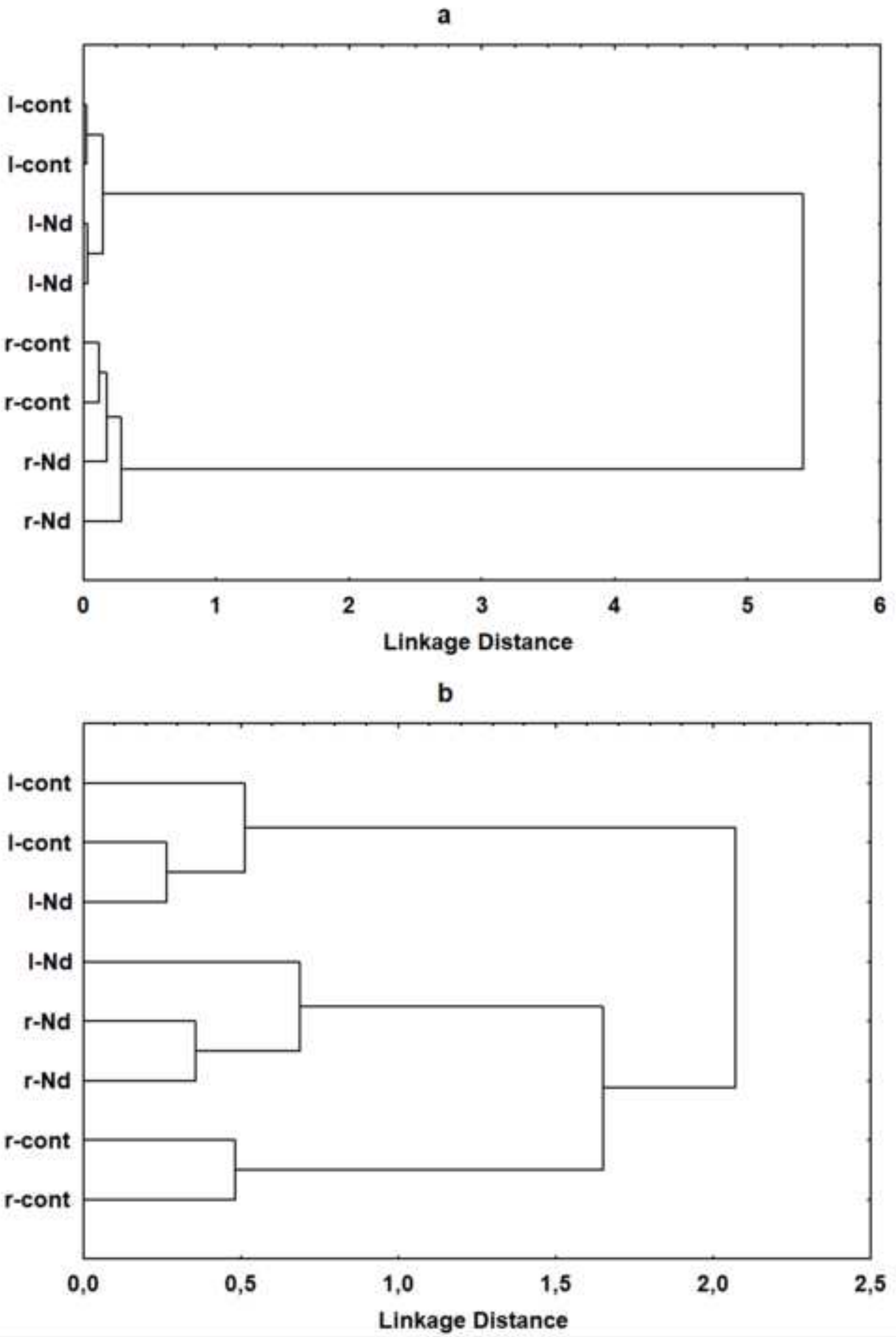
a
l-cont
l-cont
l-Nd
l-Nd
r-cont
r-cont
r-Nd
r-Nd
0
1
2
3
4
5
6
Linkage Distance
b
l-cont
l-cont
l-Nd
l-Nd
r-Nd
r-Nd
r-cont
r-cont
0,0
0,5
1,0
1,5
2,0
2,5
Linkage Distance

Table 1 Mean concentrations (n=3) ± SD of elements in wheat seedlings.
1 – control, 2 - the growth medium was spiked with $NdBr_3$ x $6H_2O$

Element	Roots (water-grown plants)		Roots (soil-grown plants)	
	1	2	1	2
Na,%	3.6±0.4[a]	3.2±0.3[a]	0.27±0.04	0.27±0.03
Mg,%	0.41±0.04[a]	0.53±0.04[a]	2.80±0.20	2.92±0.19
P,%	3.03±0.15*[a]	1.27±0.12[a]	0.55±0.01	0.48±0.02
Cl,%	0.93±0.01*	0.38±0.01[a]	1.08±0.05	0.93±0.04
K,%	1.72±0.09[a]	2.22±0.20[a]	2.89±0.12	3.26±0.13
Ca,%	0.48±0.03*[a]	0.20±0.03	0.13±0.01	0.14±0.03
Zn, mg kg^{-1}	37.1±4.6[a]	45.4±4.5[a]	25.9±1.9	30.6±2.4
Br, mg kg^{-1}	29.2±0.4*	6280±106[a]	28.6±1.4*	769±10
I, mg kg^{-1}	1.49±0.10	1.52±0.08[a]	1.31±0.07*	0.64±0.05
Nd, mg kg^{-1}	0.29±0.02*	984±13[a]	0.40±0.15*	19.5±0.7
	Leaves (water-grown plants)		Leaves (soil-grown plants)	
Na,%	0.64±0.05[a]	0.60±0.02[a]	0.29±0.01	0.28±0.02
Mg,%	0.20±0.04[a]	0.14±0.02[a]	0.40±0.02	0.38±0.01
P,%	3.17±0.25[a]	2.60±0.18[a]	1.1±0.1	1.2±0.1
Cl,%	1.05±0.02*[a]	0.28±0.02[a]	1.53±0.05	1.28±0.02
K,%	4.07±0.21[a]	4.03±0.18[a]	7.43±0.25	6.72±0.16
Ca,%	0.26±0.04[a]	0.37±0.07[a]	0.055±0.002	0.054±0.001
Zn, mg kg^{-1}	37.4±2.5[a]	42.8±2.5[a]	48.5±1.5	56.1±1.9
Br, mg kg^{-1}	86.1±4.0*[a]	3351±50[a]	31.0±1.0*	1131±43
I, mg kg^{-1}	0.15±0.04[a]	0.22±0.04	0.25±0.02	0.23±0.02
Nd, mg kg^{-1}	0.29±0.01*	63.2±3.0[a]	0.29±0.02*	0.54±0.04

* Differences between plants grown in control and in contaminated by bromide media are statistically significant ($P<0.05$). [a] Differences between plants grown in water and in soil are statistically significant ($P<0.05$).

Table 2 Ratios of K/Na and Ca/Mg in wheat seedlings grown in water and soil.
1 – non-contaminated media, 2 – contaminated by bromide of Nd media

	Roots			
	Water-grown		Soil-grown	
	1	2	1	2
K/Na	0.48	0.69	10.7	12.1
Ca/Mg	1.2	0.38	0.05	0.05
	Leaves			
K/Na	6.4	6.7	26	24
Ca/Mg	1.3	2.7	0.14	0.14