Environmental Science and Pollution Research
https://doi.org/10.1007/s11356-021-18247-y

RESEARCH ARTICLE

Accumulation of scandium, cerium, europium, hafnium, and tantalum in oats and barley grown in soils that differ in their characteristics and level of contamination

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Received: 15 February 2021 / Accepted: 16 December 2021

Abstract

Up to now, information about biogeochemistry of many trace elements is scarce. Meanwhile, all the elements are always present in soil and plants. It may be suggested that the trace elements also play certain role in the biogeochemical processes. The aim of the research was to study bioaccumulation of poorly investigated trace elements (scandium, cerium, europium, hafnium, and tantalum) and well-known elements (chromium, iron, cobalt, zinc, and arsenic) in two crops, oats and barley, and examine how these elements interact with each other as they absorbed by plants. The plants were grown in the soils that differed in their parameters and in level of contamination. Although oats and barley are botanically similar and were grown under the same conditions, the plants differed in the ability to accumulate many elements. The uptake of the elements by the plants also depended on type of soil. For example, concentrations of Cr, Fe, Co, As, Sc, Ce, Eu, Hf, and Ta in roots of the oats grown in slightly contaminated soil were much higher as compared to the concentrations of the elements in roots of the barley grown in the same soil. In leaves of the oats grown in moderately contaminated soil, the concentrations of Cr, As, Ce, Eu, and Ta were statistically significantly higher than those in leaves of the barley grown in the soil. In soils and in plants, relationships between elements were both similar and different. A statistically significant correlation was found between the poorly investigated trace elements and well-studied elements.

Keywords Poorly studied trace elements · Heavy metals · Phytoextraction · Oats · Barley · Neutron activation analysis

Introduction

It is commonly accepted that only a small part of elements are needed for normal plant development. These are the following elements: carbon, hydrogen, oxygen, nitrogen, sulfur, phosphorus, boron, silicon, potassium, sodium, calcium, magnesium, manganese, chlorine, iron, copper, zinc, and molybdenum (Kirkby 2012). This short list of biologically essential elements can be found in numerous publications. Since the last century, another group of elements, the so-called heavy metals (HM), has attracted considerable interest of researchers. In spite of the name, not only metals but also metalloids are included in the group. The list of the HM is even shorter and usually includes chromium, nickel, copper, zinc, arsenic, selenium, cadmium, mercury, lead, and uranium. Over the past decades, a great body of experimental material on environmental chemistry of the elements presented in the two groups has been published (Ligero and Lluch 1982; Gerritse et al. 1983; Bouhafa et al. 2018; Wang et al, 2018). On the other hand, the biogeochemistry of many other elements has not yet attracted much attention. Meanwhile, all the elements can also be found in soil and plants (Yamasaki et al. 2001; Aceto et al. 2019).

Contrary to the generally recognized opinion, it may be assumed that all elements are involved in the biogeochemical processes. It can be stated that our knowledge of biological role of one or another element is still in its infancy. This especially concerns trace elements that usually present in the environment at low concentrations. An insufficient quality of analytical techniques that are applied for elemental analysis is probably one of the reasons why information about significance or toxicity of the elements is still limited. With development of new methods of analysis, the information

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on biogeochemistry of previously poorly studied ultratrace elements (UTE) will undoubtedly grow.

This assumption is supported by experimental data reported during the last years. In particular, this concerns publications on bioaccumulation of antimony (Feng et al. 2013; Pierart et al. 2015; Li et al. 2018; Mykolenko et al. 2018; Zhu et al. 2020), rare earth elements (Brioschi et al. 2013; Migaszewski and Gałuszka 2015; Gwenzi et al. 2018; Kovaříková et al. 2019; Squadrone et al. 2020), thorium (Yan 2016; Soudek et al. 2019; Popic et al. 2017), bromine (Huang et al. 2011; Shtangeeva et al. 2017; Couto et al. 2018), gold (Taylor et al. 2014; Luo and Cao 2018; Ahmeda et al. 2020), and thallium (Krasnodębska-Ostręga et al. 2012; Sasmaz et al. 2016; Rader et al. 2019). Although a certain part of research has been moved to the investigation of "new" trace and ultratrace elements, information on biogeochemistry of the elements is still scarce and often contradictory. This can also be due to complicated biogeochemical processes and various factors affecting uptake of the trace elements. Moreover, in some cases, comparison of experimental results can be difficult because different researchers use different approaches for sampling and preparation of samples for analysis. As a consequence, conclusions on results of similar experiments sometimes can differ.

In addition, routine analytical techniques currently used for elemental analysis do not always allow determining low concentrations of some trace elements. Among other available methods, neutron activation analysis (NAA) is one of the most promising analytical techniques for determination of poorly studied trace elements. The NAA enables to get information about concentrations of up to 40 elements in one sample without pre-treatment of the sample before analysis (Munita et al. 2019). The latter option is very important, since any additional step used before determining very low concentrations of elements can lead to unwanted analytical errors and, as a consequence, to incorrect results of the analysis.

For our research, several trace elements that are not so widely present in scientific reports were selected. These are scandium (Sc), cerium (Ce), europium (Eu), hafnium (Hf), and tantalum (Ta). Two of the elements, Ce and Eu, have received more attention of researchers, especially in last decade (Wang et al. 2012; Shtangeeva 2014; Ramírez-Olvera et al. 2019; Krzciuk and Gałuszka 2020). Nevertheless, it was decided to include the elements in the research since they present an additional interest in the biogeochemical studies: both Eu and Ce have an ability to change their valence depending on the environmental situation (Er Tian et al. 2003; Pulido-Reyes et al. 2015), and therefore can be used as specific indicators of the environmental state. The use of Sc, Ce, Eu, Hf, and Ta in the global industry has grown steadily in recent years (Binnemansand Jones 2015; Dahle and Arai 2015; Agrawal et al. 2021; Botelho Junior et al. 2021; Hu et al. 2021). It can be expected that their concentrations in the environment can increase over time as happened in the last century with various compounds of now well-known HM. It would be useful to start in advance to study possible effects of bioaccumulation of the poorly investigated elements on the environment in order to be able to predict possible negative impacts in the future.

Information on Sc, a trace element that like Ce and Eu, also belongs to the group of rare earth elements (REEs), is scarce. Usually, Sc is outside of consideration in the projects on biogeochemistry of the REEs. Until now, one can often find in the literature the statement that Sc is non-essential and non-toxic to plants because its concentration in the plants is very low (Nordløkken et al. 2015; Minganti and Drava 2018). Nevertheless, it was shown that even insignificant variations in the concentration of Sc in the growth medium can cause negative consequences for the plant development (Shtangeeva et al. 2004). On the other hand, Elbasan et al. (2020) reported about positive effects of Sc on *Oryza sativa*.

Information on biogeochemistry of Hf and Ta is rather scarce. It is necessary to mention an extensive review on Ta in the environment published by Filella (2017). But in this work, the data on Ta in soil are described only briefly, and there is no information on Ta in plants. The author made the following conclusion: Ta has no biological role and its ecotoxicological effects are unknown. Compared to plants, more data can be found on distribution of Hf and Ta in soil. However, in many cases researchers, even if they identify these trace elements in the soil and plant samples along with other elements, simply mention that Hf and Ta were found in the samples (Wasim et al. 2016; Messaoudi and Begaa 2018; Anjum et al. 2019; Kumar et al. 2021).

As was reported, the concentrations of one or even several elements in the plants that belong to different botanical classes can differ significantly (Broadley et al. 2001; Reimann et al. 2007; White 2018). It was suggested that different plant species may have their own characteristic concentrations of elements even if the plants grow under the same natural conditions. It would be not only interesting, but also important to compare how similar plant species will uptake different elements in the case when they grow under absolutely the same conditions but in different types of soil. In the present work, two widespread agricultural crops—oats and barley—were compared. These two plants are botanically closely related. (Both belong to subfamily Pooideae and differ only at the genus level.)

Taken into account the current situation in many regions, it would be interesting to compare uptake of the poorly investigated trace elements together with well-studied toxic elements using different plant species grown in different soils. The aim of the research was to study how two important and widely grown crops (oats and barley) growing in the soils having distinct parameters and also characterized by different level of polymetallic contamination will accumulate both TM and UTE. The other purposes were to examine the interactions among the elements in soils and in different plant parts and to assess the similarities and differences in the biogeochemistry of the HM and UTE.

Materials and methods

Experimental design

Soil for the experiment was collected in St. Petersburg, Russia, from three sites that differed in the level of contamination. Site 1 was located in a park far from any source of contamination. Site 2 was near street with moderate traffic. Site 3 was arranged near a factory, close to a street with heavy traffic. Soil samples were taken from upper (0–10 cm) soil horizon. Main parameters of the soils are shown in Table 1. The soils collected from the three sites were placed into ceramic pots (volume of 5 kg). To exclude an additional source of possible impact on the uptake of elements by plants, no fertilizers were applied to the soils. Seeds of oats *Avena Sativa* L. cultivar Argamak and barley *Hordeum vulgare* L. cultivar Sonet were germinated on a moist filter paper during 5 days. The germinated seedlings were transferred to the pots (~ 20 seedlings in a pot). Oats and barley were grown in separate pots in a naturally illuminated greenhouse. Temperature inside the greenhouse was typically 25 °C during the day and 22 °C at night. The experiment was performed in triplicate. After 18 days, the plants and rhizosphere soil were collected. Roots were separated from leaves, and plants were carefully washed. Then, the soil and plant samples were dried at room temperature up to constant weight.

Elemental analysis

The concentrations of five HM (chromium (Cr), iron (Fe), cobalt (Co), zinc (Zn), and arsenic (As)) and five UTE (Sc, Ce, Eu, Hf, and Ta) were determined by instrumental neutron activation analysis. Plant and soil samples were weighed and placed in ampoules made of super pure quartz. Each sample consisted of at least six plant (or soil) samples collected simultaneously from the same place. Mass of the samples was ~ 100 mg. The plant and soil samples and certified reference material (CRM) Tomato Leaves 1573a (National Institute of Standards and Technology, Gaithersburg, MD, USA) were irradiated during 18 h in a nuclear reactor with a thermal neutron flux 4×10^{13} n cm^{-2} s^{-1}. The irradiated samples were measured by a Ge(Li) detector two times, within 1 and 3 weeks after the end of irradiation. The quality of analysis was assured with help of the CRM that was analyzed together with plant and soil samples. The differences between certified and measured concentrations of elements were less than 5%.

Table 1 Texture, pH (1:2.5 H_2O) and concentrations of exchangeable cations of the soils collected from three experimental sites

	Site 1	Site 2	Site 3
Texture	Sandy clay loam	Loam	Loamy sand
pH	7.25	7.6	7.6
Mg, mg kg^{-1}	685	135	170
K, mg kg^{-1}	1160	340	800
Ca, mg kg^{-1}	2510	1865	1925

Statistical analysis

A multivariate statistical analysis of experimental data was carried out using Statistica for Windows 6.00 Software package (StatSoft, Tulsa, OK, USA). The normality of the distribution of elements in the soil and plant samples was checked by the Shapiro–Wilk's test. Prior to the statistical analysis, the outlier data were excluded from the calculations. We calculated mean concentrations of elements and performed analysis of variances to estimate statistically significant ($P < 0.05$) differences between groups of the samples. Pearson correlation analysis and principal component analysis (PCA) were conducted to study the main factors that can affect the distribution of elements in plants and soils, and to separate samples according to concentrations of different elements. The data for the PCA were normalized to unit concentration to avoid misclassifications caused by different order of magnitudes of variables.

Results and discussion

Distribution of elements in soils and in plants

The main characteristics of the soils at the three sites were rather different (Table 1). At the sites selected for the research, the priority HM was Cr, Fe, Co, Zn, and As. The concentrations of the elements were the lowest in the soil collected from site 1 (the least contaminated) and the highest in the soil collected from site 3 (moderately contaminated) (Fig. 1). The differences between concentrations of the HM in the soils were statistically significant ($P < 0.05$). The only exception was Co; its concentration was higher in the soil collected from site 2 (slightly contaminated) than in the soils collected from site 3 and especially from site 1. A similar distribution was demonstrated by Sc and Eu (Fig. 2). The concentrations of Co, Sc, and Eu in the soil collected from site 2 were statistically significantly ($P < 0.05$) higher as

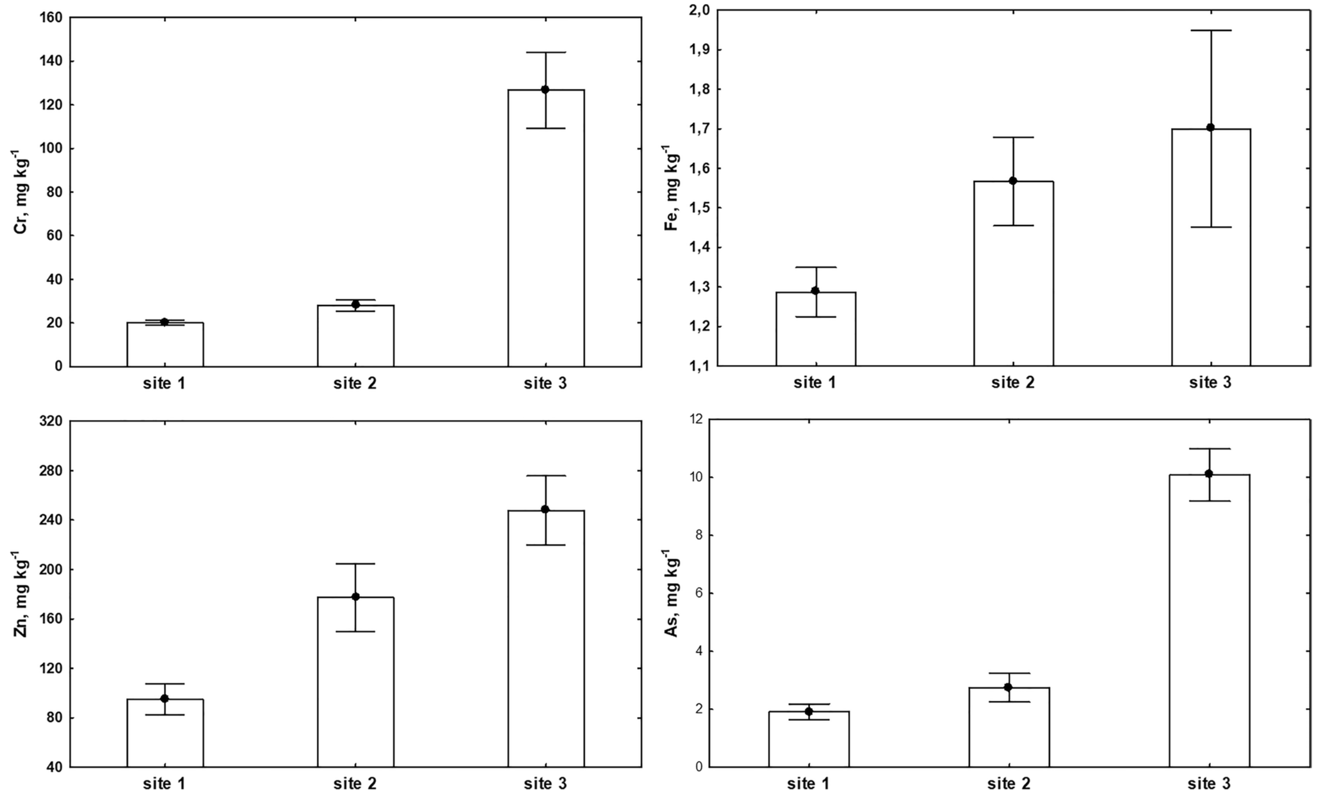

Fig. 1 Mean concentrations ± SD of Cr, Fe, Zn, and As in the soils collected from different sites

compared to the concentrations of the elements in the soils taken from sites 1 and 3. Probably, this can be explained by the fact that Co, Sc and Eu are compatible trace elements (Wörrier et al. 1983). On the other hand, the lowest concentrations of Ce, Hf, and Ta were found in the soil collected from site 2 (Fig. 3). The differences between concentrations of Ce, Hf, and Ta in the soils collected from sites 2 and 3 were statistically significant ($P < 0.05$). Except for Hf, the differences between concentrations of the UTE in the soils taken from sites 1 and 2 were also statistically significant ($P < 0.05$). Similar behavior of the three trace elements may be associated with a good biocompatibility of Hf and Ta (Matsuno et al. 2001). It is also known that Ta and Ce are among main components of mineral euxenite (Škoda and Novák 2007). This mineral is commonly found in different soils (Li and Zhou 2020). Therefore, one would expect some similarity in the environmental chemistry of the elements.

Mean concentrations of elements in roots and leaves of oats *Avena Sativa* L. and barley *Hordeum vulgare* L. grown in the soils collected from the three sites are shown in Table 2. As might be expected, roots of the plants grown in the soils collected from sites 2 and 3 had higher concentrations of some HM. For example, the concentrations of Fe, Co, and As in roots of the oats grown in the soil collected from site 1 were statistically significantly ($P < 0.05$) lower than the concentrations of the elements in roots of the oats grown in the soils collected from site 2 and site 3. Differences between concentrations of HM in roots of the barley grown in the soils collected from different sites were less noticeable. The concentration of Cr in roots of the barley grown in the soil collected from site 2 was lower as compared with Cr content in roots of the barley that grew in the soils collected from sites 1 and 3 (statistically significant differences were observed only between roots of the barley grown in the soils taken from sites 2 and 3). The concentration of As was the lowest in roots of the barley grown in the soil collected from site 1, but statistically significant differences were found only between As concentrations in roots of the barley grown in the soils collected from site 1 and site 3.

The concentrations of UTE in roots of the oats and barley grown in different soils were also different. In roots of the oats grown in the soil collected from site 2, the concentrations of Sc and Ce were statistically significantly ($P < 0.05$) higher than concentrations of the elements in roots of the oats grown in the soils taken from sites 1 and 3. On the other hand, in roots of the barley grown in the soils collected from different sites, the differences between Sc concentrations were statistically insignificant, and concentration of Ce was almost the same regardless of the soils where barley was grown. The concentration of Hf in

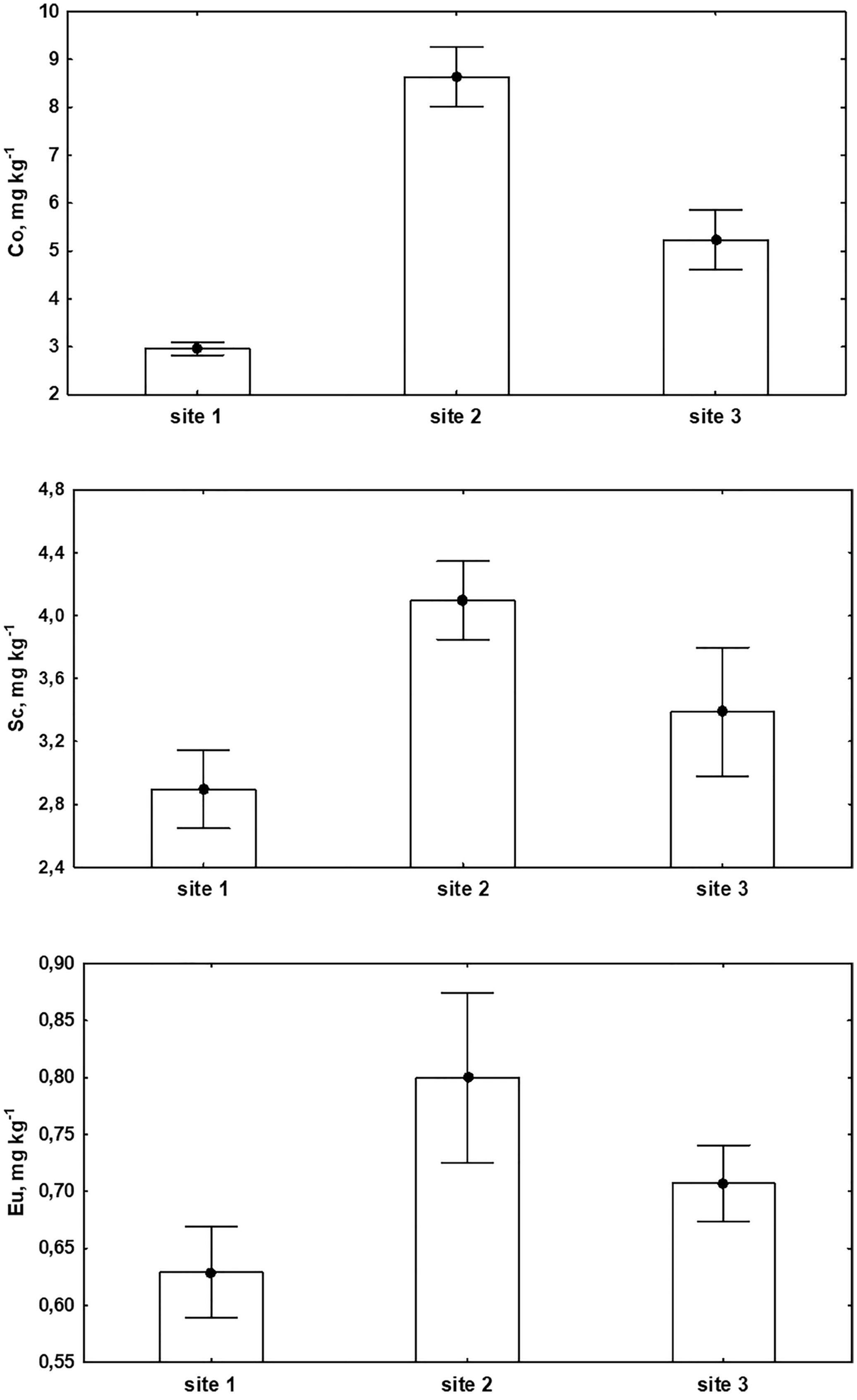

Fig. 2 Mean concentrations ± SD of Co, Sc, and Eu in the soils collected from different sites

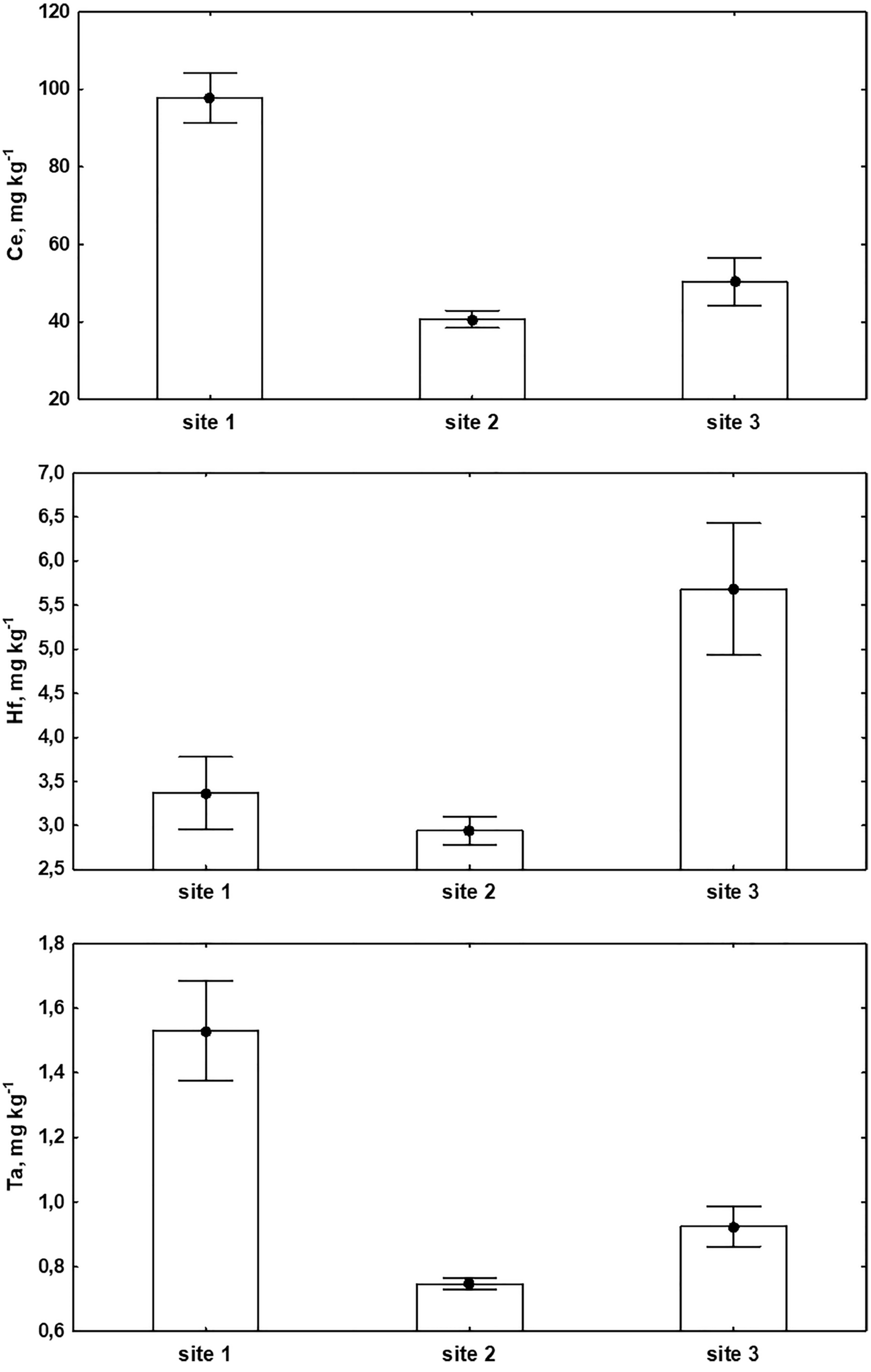

Fig. 3 Mean concentrations ± SD of Ce, Hf, and Ta in the soils collected from different sites

Table 2 Mean concentrations (mg kg^{-1}) ± SD of elements in roots and leaves of oats and barley grown in the soils collected from site 1, site 2, and site 3

	Oats			Barley		
	site 1	site 2	site 3	site 1	site 2	site 3
Roots						
Cr	7.4 ± 1.4	8.8 ± 2.8*	10.7 ± 4.1	5.7 ± 0.3	3.0 ± 0.2[f]	8.9 ± 2.8
Fe	607 ± 35[ac]	2244 ± 870*	1175 ± 247	757 ± 462	716 ± 165	1063 ± 667
Co	0.35 ± 0.07[ac]	2.3 ± 0.9*	1.98 ± 0.31	0.46 ± 0.28	0.65 ± 0.34	3.8 ± 3.2
Zn	155 ± 23*	193 ± 17	202 ± 2	244 ± 38	221 ± 91	285 ± 123
As	0.22 ± 0.07[ac]	1.7 ± 0.4*[e]	0.73 ± 0.23	0.21 ± 0.02[d]	0.33 ± 0.13	0.65 ± 0.23
Sc	0.11 ± 0.01[a]	0.37 ± 0.01*[e]	0.17 ± 0.03	0.15 ± 0.04	0.23 ± 0.04	0.15 ± 0.02
Ce	1.9 ± 0.7[a]	3.8 ± 0.5*[e]	2.0 ± 0.5	1.8 ± 0.7	1.8 ± 0.3	1.7 ± 0.5
Eu	0.07 ± 0.01*	0.08 ± 0.02*	0.04 ± 0.01*	0.010 ± 0.001	0.009 ± 0.001	0.017 ± 0.004
Hf	0.50 ± 0.09	0.70 ± 0.11*	0.46 ± 0.17	0.50 ± 0.07[b]	0.35 ± 0.33[c]	0.62 ± 0.08
Ta	0.59 ± 0.26	0.78 ± 0.19*	0.73 ± 0.23	0.30 ± 0.16	0.15 ± 0.05	0.45 ± 0.13
Leaves						
Cr	1.4 ± 0.1[c]	1.7 ± 0.5[e]	4.7 ± 0.7*	1.4 ± 0.1	1.7 ± 0.2	1.6 ± 0.5
Fe	127 ± 10	151 ± 43	141 ± 33	140 ± 41	107 ± 8	117 ± 11
Co	0.04 ± 0.01[ac]	0.08 ± 0.03	0.12 ± 0.04	0.09 ± 0.07	0.06 ± 0.01	0.10 ± 0.07
Zn	46.4 ± 6.4*	53.1 ± 16.2*	55.4 ± 10.4*	103 ± 6	95.3 ± 11.6	105 ± 16
As	0.06 ± 0.02[c]	0.08 ± 0.05[c]	0.27 ± 0.07*	0.11 ± 0.05	0.11 ± 0.03	0.10 ± 0.07
Sc	0.016 ± 0.001[a]	0.027 ± 0.004*[e]	0.0018 ± 0.003	0.02 ± 0.01	0.019 ± 0.002	0.018 ± 0.003
Ce	0.43 ± 0.11	0.52 ± 0.15	0.36 ± 0.04*	0.50 ± 0.20	0.37 ± 0.13	0.22 ± 0.06
Eu	0.013 ± 0.001*[c]	0.02 ± 0.01[e]	0.11 ± 0.03*	0.004 ± 0.001[b]	0.019 ± 0.002[f]	0.002 ± 0.001
Hf	0.14 ± 0.01*[c]	0.16 ± 0.03	0.26 ± 0.06	0.17 ± 0.01[d]	0.17 ± 0.01[f]	0.25 ± 0.03
Ta	0.14 ± 0.02[ac]	0.25 ± 0.05*	0.25 ± 0.05*	0.10 ± 0.06	0.10 ± 0.05	0.10 ± 0.04

* Differences between concentrations of elements in oats and barley collected from the same site are statistically significant ($P < 0.05$). [a] Differences between concentrations of elements in oats grown in the soil collected from sites 1 and 2 are statistically significant ($P < 0.05$). [b] Differences between concentrations of elements in barley grown in the soil collected from sites 1 and 2 are statistically significant ($P < 0.05$). [c] Differences between concentrations of elements in oats grown in the soil collected from sites 1 and 3 are statistically significant ($P < 0.05$). [d] Differences between concentrations of elements in barley grown in the soil collected from sites 1 and 3 are statistically significant ($P < 0.05$). [e] Differences between concentrations of elements in oats grown in the soil collected from sites 2 and 3 are statistically significant ($P < 0.05$). [f] Differences between concentrations of elements in barley grown in the soil collected from sites 2 and 3 are statistically significant ($P < 0.05$)

roots of the barley that grew in the soil collected from site 2 was the lowest ($P < 0.05$) as compared to concentration of Hf in roots of the barley grown in the soils collected from sites 1 and 3. Similar trend was also observed for Ta, but in this case, the differences were not statistically significant.

Mean concentrations of Cr in leaves of the oats grown in the soils collected from sites 1 and 2 were similar and statistically significantly ($P < 0.05$) lower than in leaves of the oats grown in the soil collected from site 3. The same situation was observed for As. The concentration of Co in leaves of the oats grown in the soil collected from site 1 was statistically significantly ($P < 0.05$) lower than in leaves of the oats that grew in the soils collected from sites 2 and 3. The concentrations of all five HM in leaves of the barley grown in the soils collected from the different sites were rather similar.

It can be expected that the accumulation of the HM in the plants grown in the soil collected from site 3 might result in suppression of growth of the plants. Such a tendency was observed for roots and leaves of the oats grown in the contaminated soil. However, the differences between biomasses of the plants grown in the soils collected from the different sites were statistically insignificant.

The concentration of Sc was the highest ($P < 0.05$) in leaves of the oats grown in the soil collected from site 2. The concentration of Eu was the lowest in leaves of the oats that grew in the soil collected from site 1, higher in leaves of the oats grown in the soil collected from site 2, and the highest in leaves of the oats grown in the soil collected from site 3. The differences between Eu concentration in leaves of the oats grown in the different soils were statistically significant ($P < 0.05$). Similar trend was observed for Hf and to some extent for Ta. Leaves of the barley grown in the soil collected from site 2 accumulated more Eu as compared to leaves of the barley grown in other soils. The concentrations of Hf in leaves of the barley grown in the soils collected from sites 1 and 2 were the same and were statistically significantly ($P < 0.05$) lower than in leaves of the barley grown in the soil collected from site 3.

The comparison of distribution of both HM and UTE in soils and in oats and barley grown in the soils showed different reaction of similar plant species on the soil contamination. Moreover, a higher concentration of an element in soil was often not accompanied by an increase in uptake of the element by plant roots. The distribution of Ce in the soil–plant system is a good example of the phenomenon. The concentration of Ce was the highest in the soil collected from site 1, but in roots of the oats grown in the soil, its concentration was lower than in roots of the oats grown in the soils that had much lower Ce concentration. In roots of barley, the concentration of Ce was the same no matter where the plants grew.

Differences in the concentrations of elements in oats and barley

It may be suggested that in the case when the plants grow under the same conditions, their elemental composition can be similar. However, our experiment showed that concentrations of both HM and UTE in oats and barley were different. Besides, soils where the plants grow may have certain influence on the differences. For example, roots of oats and barley grown in the soil collected from site 3 differed only in the concentration of Eu, which was statistically significantly ($P < 0.05$) higher in roots of oats. In roots of the oats grown in the soil collected from site 1, the concentration of Eu was higher and the concentration of Zn was lower as compared to those in roots of the barley grown in the same soil. (The differences were statistically significant at $P < 0.05$.) The most significant differences between elemental composition of roots of oats and barley were observed when the plants grew in the soil collected from site 2. In this case, the concentrations of Cr, Fe, Co, As, Sc, Ce, Eu, Hf, and Ta were much higher in roots of oats as compared to concentrations of the elements in roots of barley (Table 2).

Compared to roots, more differences between leaves of oats and barley were observed when the plants grew in the soil collected from site 3. In this case, the concentrations of Cr, As, Ce, Eu, and Ta were higher, and the concentration of Zn was lower in leaves of oats than in leaves of barley. In leaves of the oats grown in the soil collected from site 2, the concentrations of Sc and Ta were higher and the concentration of Zn was lower than in leaves of the barley grown in the same soil. When the plants were grown in the soil collected from site 1, the concentrations of Zn and Hf were lower, and the concentration of Eu was higher in leaves of oats as compared to those in leaves of barley. As was shown above (Table 2), the differences between concentrations of the elements in oats and barley were statistically significant ($P < 0.05$).

Thus, these two similar plants are able to uptake different amounts of elements even if they grow under absolutely the same conditions. Moreover, the differences between concentrations of elements in oats and barley also depend on the soil where the plants grow. It can be assumed that genetically determined elemental composition of plants can be different not only between plant species that belong to rather different botanical classes, but can also differ even at the genus level.

The differences between concentrations of some elements in oats and barley have also been observed by other researchers. Bityutskii et al. (2017) reported about differences between concentrations of Fe, Al, and Mn in barley and oats grown under the same conditions. In particular, the concentrations of Fe and Mn were approximately two times higher in grains of barley that those in grains of oats. Bolland and Brennan (2005) found that the concentration of

P in grains of barley was also slightly higher than in grains of oats—0.32% and 0.27%, respectively. On the other hand, Chappell et al. (2017) reported about higher concentrations of K and Mn in grains of oats compared to those in grains of barley. This is an additional confirmation of the fact that several researchers performing similar experiments can obtain different results.

Principal component analysis of plant samples

Figures 4 and 5 illustrate the results of the PCA performed on the basis of concentrations of either HM or UTE in roots and leaves of oats and barley. Taken into consideration that concentrations of many elements in the plants were statistically significantly different, we could expect a good separation of oats and barley into different groups. However, this did not always happen.

When UTE were used for calculations, roots of the oats and barley that grew in the soils collected from sites 1 and 3 were well-separated. However, the separation was not so noticeable when the plants were grown in the soil collected from site 2. Europium and Sc (site 1), Sc (site 2), and Hf (site 3) were mainly responsible for the separation. When for the PCA were used HM, the best differences between roots of oats and barley were found for the plants grown in the soil collected from site 3. Chromium and Zn (site 1), Fe and Zn (site 2), and Zn (site 3) are highly correlated with the PC1 that was responsible for the separation of roots of oats and barley.

Leaves of oats and barley were separated rather well into different groups. When UTE were used for calculations, Sc and Ta (site 1), Hf and Eu (site 2), and Sc and Eu (site 3) were mainly responsible for the separation. When for the PCA were used HM, Fe and Zn (sites 1 and 2) and Zn (site 3) highly correlated with the first PC, the dominant factor responsible for the separation. It is evident that elemental composition of plants can vary depending on the plant taxa. It seems likely that the better separation of leaves of oats and barley can partly be explained by intermediate position of roots, which are sandwiched between soil and upper parts of plants. Thus, roots are under influence of both soil and plants. As a result, compared with leaves, the elemental composition of roots may be less constant. This phenomenon was also observed by other researchers (Park and Yanai 2009; Brant and Chen 2015). Perhaps, one of the possible reasons may be a high degree of translocation of elements

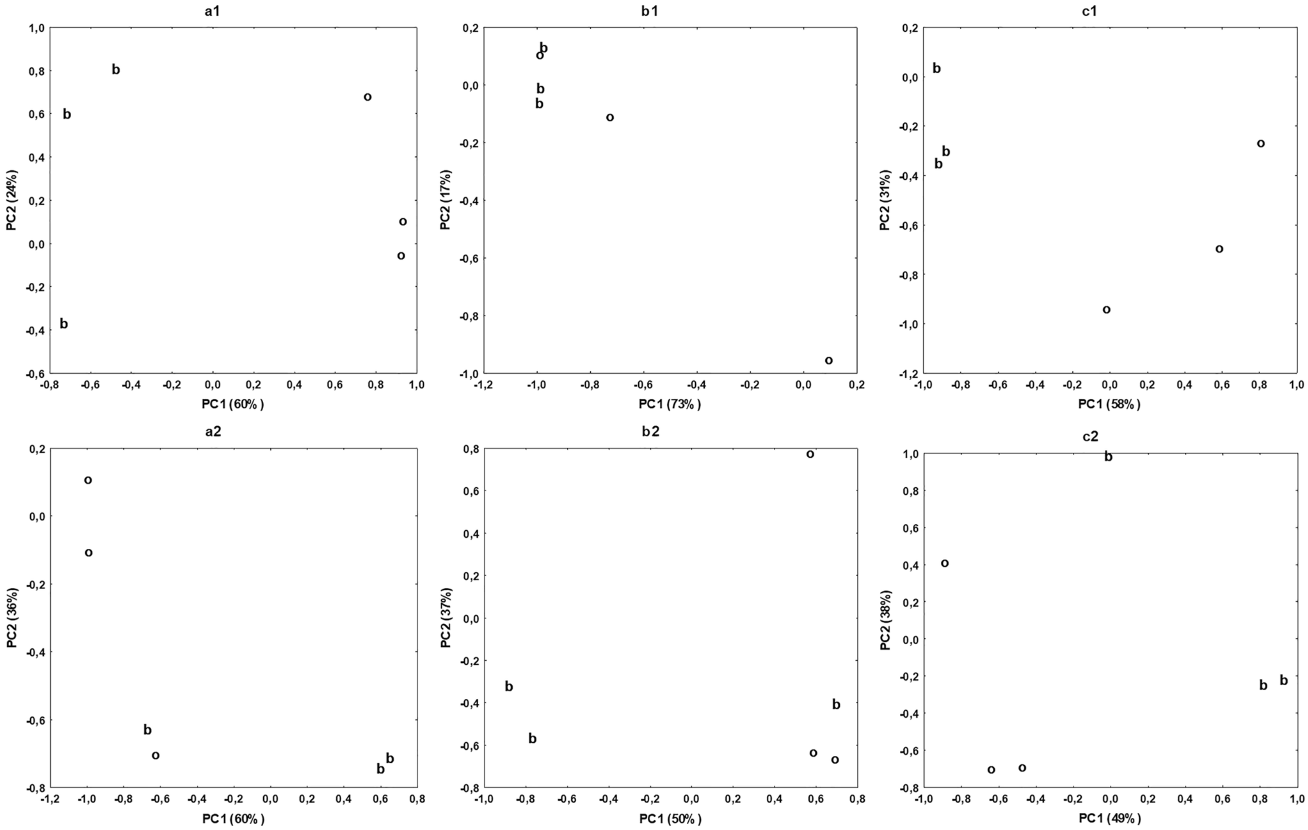

Fig. 4 Score plots of the first and second principal components of roots of oats (**o**) and barley (**b**). a—plants were grown in the soil collected from site 1, b—plants were grown in the soil collected from site 2, c—plants were grown in the soil collected from site 3. 1—for calculations which used UTE, 2—for calculations which used HM

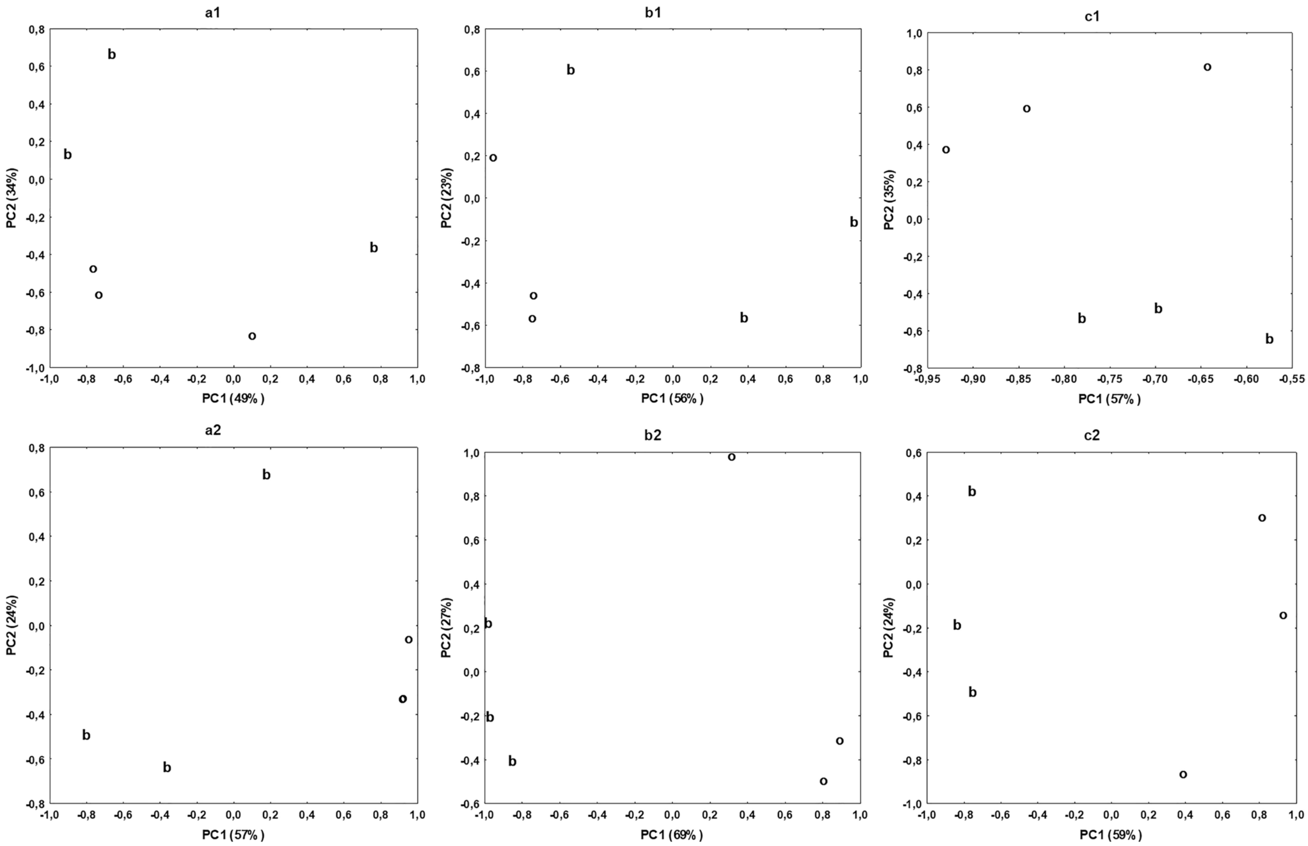

Fig. 5 Score plots of the first and second principal components of leaves of oats (**o**) and barley (**b**). a—plants were grown in the soil collected from site 1, b—plants were grown in the soil collected from site 2, c—plants were grown in the soil collected from site 3. 1—for calculations which used UTE, 2—for calculations which used HM

from the rhizosphere soil to plant roots, on the one hand, and, on the other, their low mobility from roots to aboveground parts of plants (Mazej and Germ 2009).

Correlation analysis of soil and plant samples

Table 3 shows the relationships between Cr, Fe, Co, Zn, As, Sc, Ce, Eu, Hf, and Ta in soils collected from the three sites and in different parts of the plants grown in the soils. The correlation coefficients were calculated for both plant species, not separately.

It was found that correlation between various elements in soils and plants can be both similar and different. For example, the correlation between Fe and Co was always statistically significant and positive in different parts of plants and in soils regardless of the soil type. This might be due to similar chemical characteristics of the two metals.

Iron also positively correlated with Sc in all soils, in roots of all plants, and in leaves of the plants grown in the soil collected from site 1. Iron and Sc have similar ionic radii. (Ionic radius of Fe^{3+} is 0.09 nm and ionic radius of Sc^{3+} is 0.08 nm.) In soils, these two elements are often related to each other, and Sc can replace Fe (Aide et al. 2009). A statistically significant positive correlation between these elements was also observed in different terrestrial plant species (Kanias et al. 1998; Bordean et al. 2013). Besides, similarity in the biogeochemistry of Sc and Fe has been reported in seawater organisms (Parker et al. 2016; Mellett et al. 2018).

A statistically significant ($P < 0.05$) correlation between Fe and As was found in the soil collected from site 3 and in roots and leaves of the plants grown the soil. Among other samples, a statistically significant positive correlation between these two elements was also observed in roots of the plants grown in the soil collected from site 2. Compared to other soils, the concentrations of Fe and As were the highest in the soil collected from site 3 (Fig. 1). Probably, the positive correlation between these elements might be due to the presence of some pyrite (FeS_2) in the soil. In addition to Fe, this mineral also contains certain amount of As.

A statistically significant ($P < 0.05$) correlation between Hf and Sc was found in the soil collected from site 1 and in roots and leaves of the plants grown in the soil. The correlation between these trace elements in all other samples was statistically insignificant. On the other hand, a high

Table 3 Coefficients of correlation between elements in soils and in plants

	Cr	Fe	Co	Zn	As	Sc	Ce	Eu	Hf	Ta
Soil										
Site 1										
Cr	1.00									
Fe	**0.63**	1.00								
Co	**0.82**	**0.64**	1.00							
Zn	**0.47**	-0.05	0.34	1.00						
As	0.31	0.28	0.30	0.39	1.00					
Sc	0.25	**0.63**	**0.87**	0.16	0.31	1.00				
Ce	**0.46**	0.41	0.42	-0.09	0.24	0.44	1.00			
Eu	0.32	0.40	0.22	0.12	0.08	0.43	0.44	1.00		
Hf	0.17	0.05	-0.32	-0.19	0.24	**0.47**	0.20	**0.49**	1.00	
Ta	0.18	0.36	-0.40	-0.27	0.35	0.41	0.10	-0.19	0.37	1.00
Site 2										
Cr	1.00									
Fe	0.27	1.00								
Co	0.29	**0.74**	1.00							
Zn	**0.54**	**0.64**	0.08	1.00						
As	0.10	0.42	-0.32	-0.01	1.00					
Sc	0.30	**0.81**	0.15	-0.09	0.27	1.00				
Ce	-0.17	0.34	0.20	0.18	0.36	0.42	1.00			
Eu	-0.07	0.38	**0.50**	-0.22	0.19	0.44	0.37	1.00		
Hf	-0.30	**0.52**	**0.51**	0.08	**-0.65**	0.05	0.26	0.38	1.00	
Ta	0.02	0.11	0.41	-0.03	**0.52**	0.09	0.27	**0.51**	0.36	1.00
Site 3										
Cr	1.00									
Fe	0.04	1.00								
Co	0.34	**0.67**	1.00							
Zn	0.31	0.20	0.40	1.00						
As	-0.20	**0.45**	0.34	**0.45**	1.00					
Sc	0.08	**0.70**	**0.45**	0.19	0.24	1.00				
Ce	**0.45**	0.37	0.29	-0.20	0.02	0.42	1.00			
Eu	-0.35	0.19	0.14	-0.06	-0.09	0.30	0.38	1.00		
Hf	0.29	-0.06	-0.25	0.01	-0.26	0.15	0.03	0.34	1.00	
Ta	-0.02	0.07	0.10	-0.09	-0.21	-0.15	0.26	0.33	0.28	1.00
Roots										
Site 1										
Cr	1.00									
Fe	0.20	1.00								
Co	0.16	**0.64**	1.00							
Zn	-0.05	0.12	0.42	1.00						
As	0.02	0.43	0.37	-0.02	1.00					
Sc	0.22	**0.71**	**0.67**	0.28	0.37	1.00				
Ce	-0.03	**0.74**	**0.76**	-0.22	-0.30	**0.73**	1.00			
Eu	0.27	**0.57**	**0.50**	0.18	-0.24	0.42	**0.83**	1.00		
Hf	0.01	**0.68**	**0.74**	0.25	0.03	**0.80**	**0.89**	**0.85**	1.00	
Ta	-0.23	-0.10	0.04	0.15	0.20	0.39	0.21	0.40	0.35	1.00
Site 2										
Cr	1.00									
Fe	0.42	1.00								
Co	0.37	**0.54**	1.00							
Zn	0.23	0.28	0.36	1.00						
As	-0.12	**0.70**	0.20	-0.23	1.00					

Table 3 (continued)

	Cr	Fe	Co	Zn	As	Sc	Ce	Eu	Hf	Ta
Sc	0.38	**0.74**	0.39	-0.08	0.20	1.00				
Ce	**0.64**	**0.53**	**0.55**	0.22	0.34	-0.21	1.00			
Eu	**0.59**	0.29	0.31	**-0.45**	0.05	0.19	**0.63**	1.00		
Hf	**0.81**	-0.25	-0.20	0.00	-0.30	0.17	0.28	0.26	1.00	
Ta	**0.55**	0.13	0.04	0.16	-0.26	0.35	**0.50**	0.31	0.41	1.00
Site 3										
Cr	1.00									
Fe	0.19	1.00								
Co	0.26	**0.67**	1.00							
Zn	0.28	0.23	0.31	1.00						
As	-0.25	**0.60**	0.33	0.04	1.00					
Sc	0.18	**0.67**	0.26	-0.12	**0.56**	1.00				
Ce	**0.76**	0.40	0.33	0.05	-0.09	0.24	1.00			
Eu	**0.67**	0.36	0.41	-0.03	-0.16	0.32	0.44	1.00		
Hf	**0.63**	0.32	0.10	0.15	0.03	0.12	**0.55**	-0.03	1.00	
Ta	**0.70**	-0.27	-0.06	0.26	0.08	0.25	**0.73**	0.20	0.33	1.00
Leaves										
Site 1										
Cr	1.00									
Fe	**0.49**	1.00								
Co	-0.05	**0.92**	1.00							
Zn	-0.18	0.05	0.26	1.00						
As	0.09	0.04	0.03	**0.54**	1.00					
Sc	**0.48**	**0.60**	**0.60**	0.30	0,21	1.00				
Ce	0.27	0.13	0.25	-0.32	0.17	0.38	1.00			
Eu	**-0.45**	0.43	0.28	-0.04	-0.07	**0.47**	0.39	1.00		
Hf	0.34	**0.49**	**0.52**	0.21	0.27	**0.80**	0.43	**0.85**	1.00	
Ta	-0.18	0.34	-0.02	0.11	0.33	0.26	**0.56**	**0.56**	0.38	1.00
Site 2										
Cr	1.00									
Fe	0.25	1.00								
Co	0.36	**0.63**	1.00							
Zn	0.19	0.23	0.14	1.00						
As	-0.06	0.08	0.03	0.21	1.00					
Sc	0.17	0.43	0.38	**-0.61**	0.06	1.00				
Ce	0.22	**0.54**	**0.52**	0.10	-0.31	0.40	1.00			
Eu	0.34	0.42	0.29	**-0.56**	0.13	**0.45**	**0.56**	1.00		
Hf	**0.69**	0.18	**0.50**	-0.23	0.04	0.37	0.32	0.11	1.00	
Ta	-0.05	0.21	0.36	**-0.60**	-0.20	0.27	**0.57**	**0.52**	0.36	1.00
Site 3										
Cr	1.00									
Fe	0.42	1.00								
Co	0.38	**0.49**	1.00							
Zn	0.06	0.35	0.02	1.00						
As	-0.06	**0.51**	0.19	0.24	1.00					
Sc	0.40	0.44	0.37	0.21	-0.30	1.00				
Ce	0.43	**0.47**	0.36	0.03	0.28	0.35	1.00			
Eu	**0.63**	0.36	0.28	0.18	-0.08	0.41	0.38	1.00		
Hf	**0.55**	-0.04	0.02	**0.48**	0.26	0.34	0.29	0.17	1.00	
Ta	**0.73**	0.23	0.15	0.07	0.02	0.26	0.03	**0.85**	0.25	1.00

Statistically significant ($P < 0.05$) values are shown in bold correlation between Hf and Cr was observed in roots and leaves of the plants grown in the soils collected from sites 2 and 3, but in the plants grown in the soil collected from site 1 (and also in all soils), no correlation between Hf and Cr was found. Chromium is highly correlated with Ce, Eu, Hf, and Ta in roots of the plants grown in the soils collected from sites 2 and 3, while in roots of the plants grown in the soil taken from site 1, no correlation between Cr and other elements was found. Europium is positively correlated with Hf in the soil collected from site 1 and in roots and leaves of the plants grown in the soil. However, there was no correlation between these two elements in other samples.

It is also necessary to mention about statistically significant negative correlation that was observed in few cases and mainly in the soil taken from site 2 and in the plants grown in the soil. In soil, this was a pair As and Hf; in roots—a pair Zn and Eu; in leaves, a statistically significant negative correlation was found between Zn and Sc, Zn and Eu, and Zn and Ta.

Based on the results of the correlation analysis, we can say that in many cases the same correlation between elements occurred in the soil collected from site 1 and in roots and in leaves of the plants grown in the soil, while for the soils taken from sites 2 and 3 and in the plants grown in the soils, this was less common.

Conclusions

In our experiment, two widely grown crops (oats and barley) were studied. The plants were grown in the soils that differed in the main parameters (texture, pH, and concentrations of exchangeable cations) and also in the level of contamination. The main aim of the research was to study the ability of the plants to accumulate both well-known toxic elements and also the trace elements that are poorly studied yet. The results showed that both crops were capable of accumulating various elements. The uptake of the elements depended on type of soil, level of soil contamination and was often different for oats and barley. Although oats and barley are botanically similar and were grown under the same conditions, they were able to uptake different amounts of one or another element. In some cases, the poorly investigated trace elements (Sc, Ce, Eu, Hf, and Ta) highly correlated with well-studied toxic elements such as Cr, Fe, Co, Zn, and As. Probably, this may indicate that the UTE (like the elements present in plants in higher concentrations) can also have certain contribution to the plant biogeochemistry. It can be concluded that many trace elements that occur in the environment at low concentrations and have not got yet a proper examination should also be considered as potentially toxic elements. The improvement of accuracy and sensitivity of analytical techniques used for elemental analysis of plant and soil material can help to get a new insight into the significance and/or potential toxicity of many new trace and ultratrace elements.

Authors' contribution Not applicable.

Funding Irina Shtangeeva acknowledges a partial support of this work by Russian Foundation of Basic Research (Grant No. 18–53-80010).

The author confirms that the data supporting the findings of this study are available within the article.

The author has no conflicts of interest to declare that are relevant to the content of the article. This article does not contain any studies involving animals or human participants.

Declarations

Consent to participate and consent to publish Not applicable to the manuscript.

Competing interests The author declares that she has no competing interests.

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