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Original Research

Assessment of the Impact of Soil Contamination by Potentially Toxic Elements on the Bioavailability in Barley Straw

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Abstract

Nowadays, soil contamination by risk elements from industry is a serious environmental problem. As one of the factors, it is necessary to monitor the biological availability of potentially toxic elements from soil to plants. The aim of the study is to evaluate the biological availability of the aboveground parts of barley biomass in the soil contaminated by PTEs. Biological availability was monitored for the risk elements Mo, Sr, As, and Cd. Moreover, the mutual interaction between individual soil treatments with the addition of PTEs and the content of selected risk elements (Mo, Mn, Sr, Cr, As, Cd, Pb, Cu, Zn) in barley straw was studied. Non-parametric Mann-Whitney U test was used for the assessment of statistically significant change in the biological availability of PTEs for barley straw. In many cases, a positive or negative correlation was determined between the bioavailability of metals in different variants of contamination. Mo, Sr, As, or Cd positively affected the intake of Zn into barley straw at increased concentrations in the soil. Of all the variants of contamination, Cd brought about the greatest support for the intake of the elements, which led to an increase in the intake of Mo, Sr, Cd, and Zn. On the other hand, the same element acted as a blocker of the largest number of PTEs compared to

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other variants of contamination, namely Cr, As, Pb, and Cu. For PTEs, Mo, Sr, and Cd confirmed As a blocker of intake.

Keywords: barley straw, synergism and antagonism of PTEs, nonparametric tests, soil contamination, bioavailability of agricultural plants

Introduction

Heavy metal contamination in agricultural soil has become one of the most important environmental problems for environmental and agricultural scientists [1]. Potentially toxic elements (PTEs) include metals and non-metals such as As (Arsenic), Cd (Cadmium), Mo (Molybdenum), Zn (Zinc), Pb (Lead), Hg (Mercury), Cr (Chromium), Cu (Copper), Ni (Nickel), and Se (Selenium). Due to their toxicity and long-term persistence, toxic elements seriously threaten the functioning of ecosystems [2].

Mo is a trace element found in soil and is needed for the growth of most biological organisms, including plants and animals. On the other hand, Mo toxicity in plants under most agricultural conditions is rare. In the case of tomatoes and cauliflowers, if grown on high concentrations of Mo, their leaves accumulate anthocyanins and turn purple, while the leaves of legumes turn yellow [3]. Symptoms of Mo deficiency are more commonly observed in members of the Brassicaceae family. Members of this family exhibit a range of phenotypes associated with Mo deficiency and are reproducible in other plant species within the Brassicaceae family. Common manifestations include stunted growth, lameness, twisting, curling and leaf spotting, and sometimes chlorosis, gray discoloration, and yellowing of leaves with stunted and dying seedlings [4].

Sr (Strontium) is a natural and commonly occurring alkaline earth metal [5]. Sr is not a biogenic element, but it is easily taken up by plants because it has a similar chemical composition to calcium [6]. Sr is easily transported to the shoots by xylem sap [7]. Sr binds strongly to plant cell walls, and the inclusion of strontium prevents damage to the shoots of plants grown in a calcium-deficient medium. Strontium is able to imitate the role of calcium in maintaining the integrity of the cell wall, and it supports previous studies that have shown that calcium deficiency is the result of the collapse of the cell wall of subapical cells. However, strontium can also be toxic to plants under certain conditions. Strontium accumulated in the leaves damaged various photosynthesis processes, such as energy absorption, energy transfer, and photosynthetic carbon assimilation [8].

As is an extremely lethal, ubiquitous metalloid (even in low concentrations) with a higher atomic weight that can harm living organisms [9]. As significantly reduces seed germination, morphological changes such as the number of leaves, the length of roots and shoots, and photosynthesis, which ultimately reduces yield and fruit production. As interferes with the metabolic processes of plants and focuses on growth, causing oxidative stress that often leads to cell death [10].

Cd can have a negative effect on the growth of agricultural crops at higher concentrations. According to a study [11], the weight of the above-ground parts of barley was decreased to half by soil contamination with Cd. When monitoring soil contamination by metals (Cd 3.2-106 $mg \cdot kg^{-1}$, Pb 146-3452 $mg \cdot kg^{-1}$, Zn 465-l 1375 $mg \cdot kg^{-1}$), the highest concentrations of metals were found in intact potato tubers, smooth meadow-grass, and barley straw. The observed decrease in crop yields was probably the result of a possible imbalance of nutrients rather than the phytotoxicity of metals [12]. The study declared that exposure to Cd reduced the content of chlorophyll and proteins [13]. It was confirmed that Cd inhibited the germination percentage of Phragmites australis and delayed the onset of germination in a dose-dependent manner [14].

Plants are known to absorb trace elements from contaminated soil. Approximately 450 species are even known as hyperaccumulators. In the past, microorganisms were also used for soil remediation [15]. Although they represent less than 0.2% of all known species, they have a wide taxonomic range. Coal and waste incineration, metal smelting, and car emissions are the primary anthropogenic airborne sources of toxic elements. Metals from airborne sources are usually released as particles contained in the gas stream. Metals such as Cd, As, and Pb can also escape from high-temperature activities; they can turn into oxides and condense as fine particles unless a reducing atmosphere is maintained. Chimney emissions can circulate through large areas by natural airflow until dry or wet precipitation removes them from the gas stream. Fugitive emissions are often distributed over a much smaller area. In general, concentrations of contaminants are lower in fugitive emissions compared to chimney emissions [2]. The aim of the study is to assess the biological availability of above-ground barley biomass in the soil contaminated by PTEs. Biological availability was monitored for the risk elements Mo, Sr, As, and Cd. In addition, the mutual interaction between individual soil treatments with the addition of PTEs and the content of selected risk elements (Mo, Mn, Sr, Cr, As, Cd, Pb, Cu, Zn) in the barley straw was studied.

Table 1. Agrochemical characteristics of the soil used in the experiments.

Indicator	Value
Exchange reaction ph/kcl	6.38
Humus content (%)	2.01
Phosphorus content (mg·kg^{-1})	58.60
Potassium content k (mg·kg^{-1})	188.70

Material and Methods

Variants of Soil Contamination

To set up the experiment, the so-called Mitscherlich pots, plastic and with a perforated bottom, were used. Into these containers, 6 kg of substrate consisting of soil and silica sand was weighed in a ratio of 5:1. The soil contained an upper humus horizon of modal luvisol (LMm), loam with a medium supply of basic acceptable nutrients, and a humus content of 2.1%. The agrochemical characteristics of the used soil are shown in Table 1.

Basic nutrients from NPK were added to this substrate by addition of nitrogen (N) in form of NH_4NO_3, phosphorus (P) in form of $Ca(H_2PO_4)_2 \cdot CaHPO_4$ and potassium (K) in form of 40% KCl in a ratio of 1:1.2:1.4. Intoxication solutions were added to this basic substrate according to the experimental variant in the form of Mo – $(NH_4)_6Mo_7O_{22}$, As – $NaH_2AsO_4 \cdot 7H_2O$ and Cd – $CdCl_2 \cdot 2½\ H_2O$. In the Mo and Sr variants, the dose of NH_4NO_3 was adjusted for nitrogen content, as it was present in the intoxication solution. The agrochemical characteristics of the soil used in the experiments are shown in Table 1.

Variants of the Experiment

A – NPK control
B – NPK + Mo (dose of 20 mg·kg^{-1})
C – NPK + Sr (10 mg·kg^{-1})
D – NPK + As (20 mg·kg^{-1})
E – NPK + Cd (5 mg·kg^{-1})

In a container vegetation experiment, we applied four PTEs (Mo, Sr, As, Cd) to the substrate (soil and silica sand) in quantities corresponding to the contents of concentration intervals in soils from the area of the Power Plant in Nováky – cadastral area of Osľany and Čereňany (Table 2). The measurements were carried out in five repetitions. The effect of the addition of these PTEs to the soil was observed in the interaction with the content of risk elements in aboveground biomass – straw – of barley.

Data Collection

Biomass harvesting was carried out at the stage of full physiological maturity. Each plant in the container was cut with scissors approximately 1 cm above the surface. The obtained biomass was placed on a prepared large filter paper, marked with the letter of the variant and the number of the container (there were 5 repetitions for each variant). After harvesting the biomass, the ear was separated from the stem (straw) at the site of the last internode, and then the individual parts were weighed. The obtained data were taken down.

Analysis of Straw

After the biomass collection, the obtained straw was homogenized according to the variants and containers. Firstly, the straw was cut in a special cutter, and then the cut straw was ground in finer mills. In this way, a solid matrix was prepared for further processing. After subsequent mineralization, the biological material was analyzed using the AAS method with a VARIAN AAS 24 FS absorption spectrophotometer (Australia). The results of 10 measurements in one variant expressed in mg·kg^{-1} were recorded and statistically evaluated.

Statistical Data Analysis

At the beginning of the statistical evaluation of the measured data, the basic descriptive characteristics

Table 2. Contents of PTEs from the samples from the studied areas.

Element	Average content of the element [mg·kg^{-1}]	Range of content of elements [mg·kg^{-1}]	
		$x_{min.}$	x_{max}.
Mo	20.01	1.34	49.9
Sr	9.76	5.41	13.02
As	21.04	1.45	38.18
Cd	4.91	0.37	10.21

Note: The limits are given for the content of As in clay soil (25 mg·kg^{-1}) and for Cd in clay soil (0.7 mg·kg^{-1}). Limit values of risk elements in the relation of agricultural land and plant (so-called critical values) comply with the Annexe No. 2 of the Act No. 220/2004 Coll. on the Protection and Use of Agricultural Land for As (0.4 mg·kg^{-1}) and for Cd (0.1 mg·kg^{-1}) (in compliance with the Act No. 220/2004 Coll. on the Protection and Use of Agricultural Land).

were computed. Box plots were used for their graphic presentation. Because the measured values did not meet the conditions of the parametric tests, the non-parametric Mann-Whitney U test was applied to assess significant changes in the PTEs content. The null hypothesis that the position of the two distributions is the same was tested against the alternative hypothesis about the different distributions of the data. The test statistic U works with the order of values and is approximated by a normal distribution with a modified test statistic Z of the form:

$$Z = \frac{U_1 - \frac{n_1.n_2}{2}}{\sqrt{\frac{n_1.n_2.(n_1+n_2+1)}{12}}}$$

$$U_1 = n_1.n_2 + \frac{n_1(n_1+1)}{2} - T_1$$

where n_1 is the size of the first sample, n_2 is the size of the second sample, and T_1 is the sum of the order of the values in the first sample. As the decision rule α-level of 0.05 was set in testing. Statistical software STATISTICA 14 was used for all statistical analyses [16].

Results and Discussion

Statistical comparison of the bioavailability of individual PTEs analyzed in plants depending on the variants. The description of the individual variants was provided in the Material and Methods section. To assess the effect of soil contamination with selected elements Mo, Sr, As, and Cd on their bioavailability of PTEs, we first evaluated the effect of simulated doses corresponding to the level of soil contamination on the straw production of spring barley. The results are summarized in Table 3.

The production of straw dry matter was supplemented with a one-factor analysis of variance (Table 4).

Table 3 shows that the simulated addition of all elements (Mo, Mn, As, and Cd) reduced the average straw production of spring barley. Based on the results of analysis of variance (ANOVA) (Table 4), it can be confirmed that the effect of elemental dose on dry matter straw biomass production of the cultivated plants is statistically highly significant. The added elements had a negative impact on straw phytomass production, in the order Mo>Sr>Cd = As.

Table 5 shows the average levels of added elements representing soil contamination. They show that the simulated doses of added elements caused a significant increase in the accumulation of these elements in the dry matter of spring barley straw compared to control A.

According to Table 5, the highest Mo content was observed in variant B (34.01 $mg \cdot kg^{-1}$), where this element was added in a simulated manner. The highest Sr content was observed after its addition in variant C (22.74 $mg \cdot kg^{-1}$), the most significant accumulation of As was in variant D (3.26 $mg \cdot kg^{-1}$), corresponding to its simulated addition to the soil, and the highest average Cd content was in variant E (4.14 $mg \cdot kg^{-1}$), again corresponding to the effect of its simulated addition.

In addition to the contents of the added elements, we also evaluated the accumulation of other important PTEs in the dry matter of spring barley straw. The average contents of these elements are summarized in Table 6.

After evaluating the contents of individual PTEs in the dry matter of spring barley straw, we performed

Table 3. Effect of simulated doses corresponding to the level of soil contamination on the straw production of spring barley.

Variant	Count	Spring barley straw weight in grams ($x \pm s_x$)	Percentage
A	5	36.96±1.518	100.00
B	5	32.08±7.277	86.80
C	5	32.06±10.168	86.74
D	5	29.4±8.485	79.55
E	5	29.56±9.043	79.98

Table 4. Analysis of variance for spring barley straw production in model experiments.

Source of Variation	S S	df	MS	F	P-value
Between Groups	186.622	4	46.656	6.393	0.0018
Within Groups	145.964	20	7.298		
Total	332.5864	24			

$a_{0.05} = 2.866$; $a_{0.01} = 4.431$

Table 5. The average levels of added elements representing soil contamination.

Variant	Content of the added element in straw dry matter in mg·kg^{-1} ($x \pm s_x$)			
	Mo	Sr	As	Cd
A	5.15±0.51	11.31±2.19	0.786±0.42	0.399±0.08
B	34.01±5.96	13.51±1.03	0.313±9.70	0.384±0.05
C	19.62±2.52	22.74±2.52	0.328±0.03	0.419±0.08
D	4.85±1.88	23.6±32.47	3.260±0.55	0.355±0.14
E	16.32±3.97	18.52±2.61	0.256±0.04	4.140±0.65

Table 6. Content of non-added PTEs in straw during the simulation of added metals.

Variant	Content of other PTEs in straw dry matter in mg·kg^{-1} ($x \pm s_x$)				
	Mn	Cr	Pb	Cu	Zn
A	32.33±7.24	1.20±0.36	1.08±0.54	2.99±0.48	25.46±5.58
B	31.01±3.75	0.75±0.28	1.03±0.49	2.11±0.21	63.34±4.09
C	33.18±4.19	0.58±0.23	1.18±0.39	2.45±0.26	61.46±3.26
D	36.46±2.95	0.39±0.17	0.78±0.40	1.78±0.27	61.50±4.02
E	31.04±1.30	0.40±0.14	0.39±0.24	2.20±0.14	48.34±5.69

a statistical comparison of the bioavailability of individual PTEs depending on the variants. The effect of Mo addition on the accumulation of PTEs in spring barley dry matter and their bioavailability is indicated by the results presented in Table 7 and Fig. 1.

Final parameters of the Mann-Whitney test for the comparison of variants A and B are shown in Table 3. Graphical comparison of the variants A and B for the bioavailability of all selected PTEs is shown in Fig. 1.

Compared to the control A-variant, the content of simultaneously added Mo and Zn increased significantly. The content of Cr, As, and Cu decreased slightly. However, in terms of bioavailability, the relationship between Mo and Zn is the most relevant.

Final parameters of the Mann-Whitney test for the comparison of the variants A and C are in Table 8. Graphical comparison of the variants A and C for bioavailability of all selected PTEs is shown in Fig. 2.

When evaluating the effect of simulated Sr addition, we found, on the basis of statistical analyses, that there was a demonstrable increase in simulated Sr content, but we also observed an increased accumulation of Mo and Zn. The uptake (i.e., bioavailability was affected) of Cr, As, and Cu was slightly reduced.

Table 7. Parameters of the Mann-Whitney test for the comparison of variants A and B.

PTEs	Sum of the ranks A	Sum of the ranks B	U-test	Adjusted Z	p-value	Level of significance
Mo	55	155	0	-3.75	0.000	***
Mn	116	94	39	0.79	0.427	–
Sr	77	134	22	-2.12	0.034	*
Cr	140	70	15	2.63	0.008	**
As	142	68	13	2.76	0.006	**
Cd	115	96	41	0.69	0.492	–
Pb	108	102	47	0.19	0.850	–
Cu	147	63	8	3.15	0.002	**
Zn	55	155	0	-3.74	0.000	***

Level of significance $p<0.05$*, $p<0.01$**, $p<0.001$***.

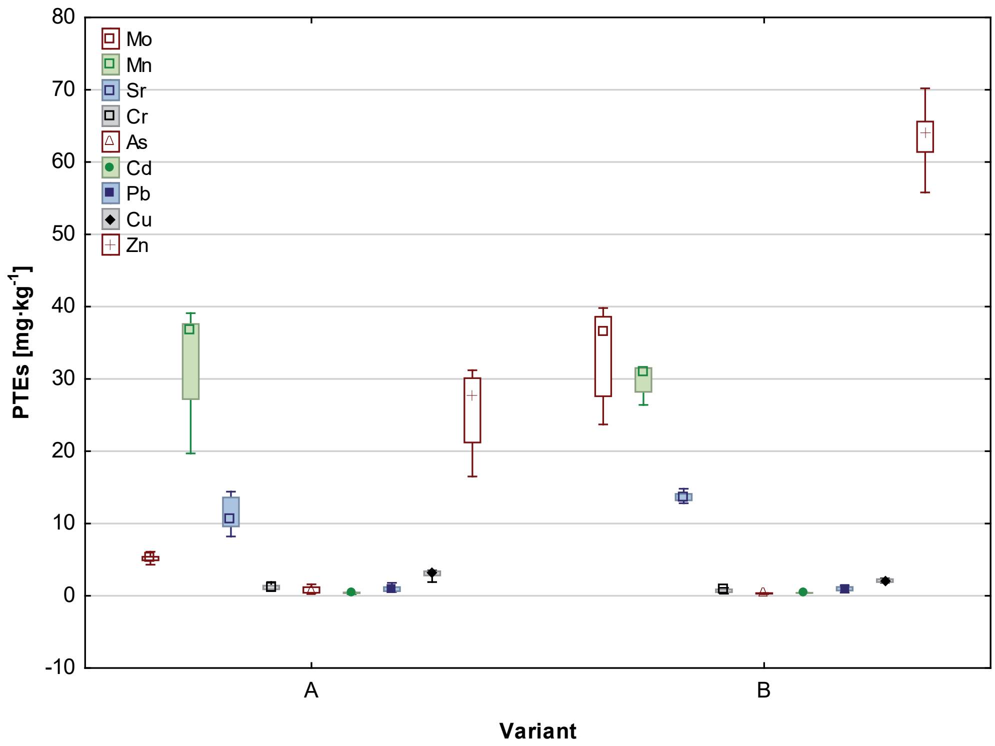

Fig. 1. Bioavailability of individual PTEs when comparing the variants A and B.

In order to compare the accumulation of PTEs in the dry matter of spring barley between variants A (control) and D (simulated addition of As) are final parameters of the Mann-Whitney test for the comparison of the variants A and D in Table 9, graphical comparison of the variants A and D for bioavailability of all selected PTEs are shown in Fig. 3.

The above results show that the application of As in the simulation significantly increased its accumulation, as well as that of Zn and Mn to a lesser extent. At the same time, a significant decrease in the average Cr content is evident.

In variant E, the effect of elevated Cd concentrations was modeled. Final parameters of the Mann-Whitney test for the comparison of the variants A and E are in Table 10, and a graphical comparison of the variants A and E for bioavailability of all selected PTEs is shown in Fig. 4.

From the results presented, it is again evident that the simulated dose of Cd significantly increased its accumulation in the straw dry matter of spring barley. At the same time, however, the contents of Mo, Sr, and Zn were significantly increased, and, on the contrary, the contents of Cr and Pb were decreased.

Table 8. Parameters of the Mann-Whitney test for the comparison of the variants A and C.

PTEs	Sum of the ranks A	Sum of the ranks C	U-test	Adjusted Z	p-value	Level of significance
Mo	55	155	0	-3.75	0.000	***
Mn	102	109	47	-0.23	0.820	–
Sr	55	155	0	-3.74	0.000	***
Cr	150	60	5	3.39	0.001	**
As	152	59	4	3.48	0.000	***
Cd	99	111	44	-0.42	0.676	–
Pb	94	116	39	-0.79	0.427	–
Cu	141	70	15	2.65	0.008	**
Zn	55	155	0	-3.74	0.000	***

Level of significance $p<0.05$*, $p<0.01$**, $p<0.001$***.

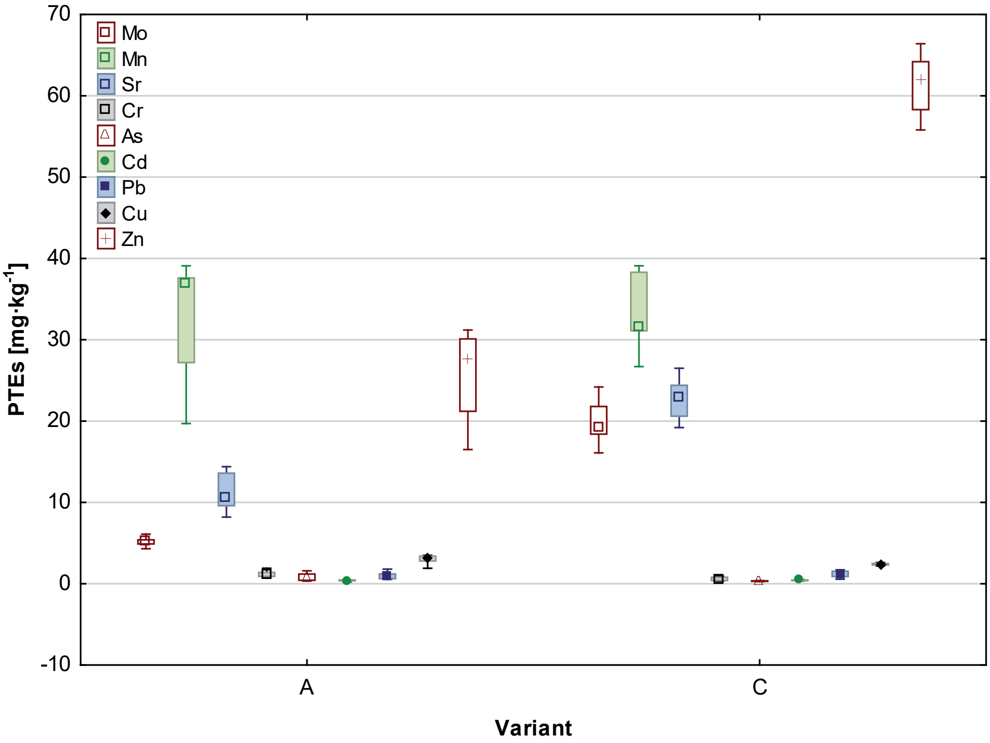

Fig. 2. Bioavailability of individual PTEs when comparing the variants A and C.

The element Mo is an important microelement that has an indispensable function in nitrogen metabolism in the soil-plant system [17]. It is part of the enzyme complexes responsible for the conversion of ammoniacal forms of nitrogen to nitrites and then to nitrates in plants; it is involved in the processes of incorporation of nitrogenous substances into amide bonds. The importance of Mo and its diverse role in plant physiology was studied by [18], who pointed out its contribution to the metabolism of nitrogen within a plant. It also significantly facilitates the improvement of abiotic stress tolerance to salinity and water stress in plants. However, increased Mo concentrations can have a negative effect on the growth and development of wheat (*Triticum aestivum* L.). This is reflected in a decrease in production, but also in increased accumulation [19, 20]. In our study, however, we focused on a related type of cereals: barley (*Hordeum vulgare* var. *distichon* L.).

Its active excess was manifested not only by an increase in Mo content in the dry matter of the straw of barley that was experimentally grown, but also by an increased uptake of Sr and Zn into the plant organism (increased concentration of these elements) and at the same time, blocking the uptake of elements such as Cr, Cu, and As (decreased concentration of these elements in the dry matter of the barley straw).

Table 9. Parameters of the Mann-Whitney test for the comparison of the variants A and D.

PTEs	Sum of the ranks A	Sum of the ranks D	U-test	Adjusted Z	p-value	Level of significance
Mo	124	86	31.0	1.40	0.161	–
Mn	93	117	38.0	-0.87	0.384	–
Sr	79	131	24.0	-1.93	0.054	–
Cr	155	56	0.5	3.72	0.000	***
As	55	155	0.0	-3.74	0.000	***
Cd	124	87	31.5	1.36	0.172	–
Pb	121	89	34.0	1.17	0.241	–
Cu	142	68	13.0	2.77	0.006	**
Zn	55	155	0.0	-3.74	0.000	***

Level of significance p<0.05*, p<0.01**, p<0.001***.

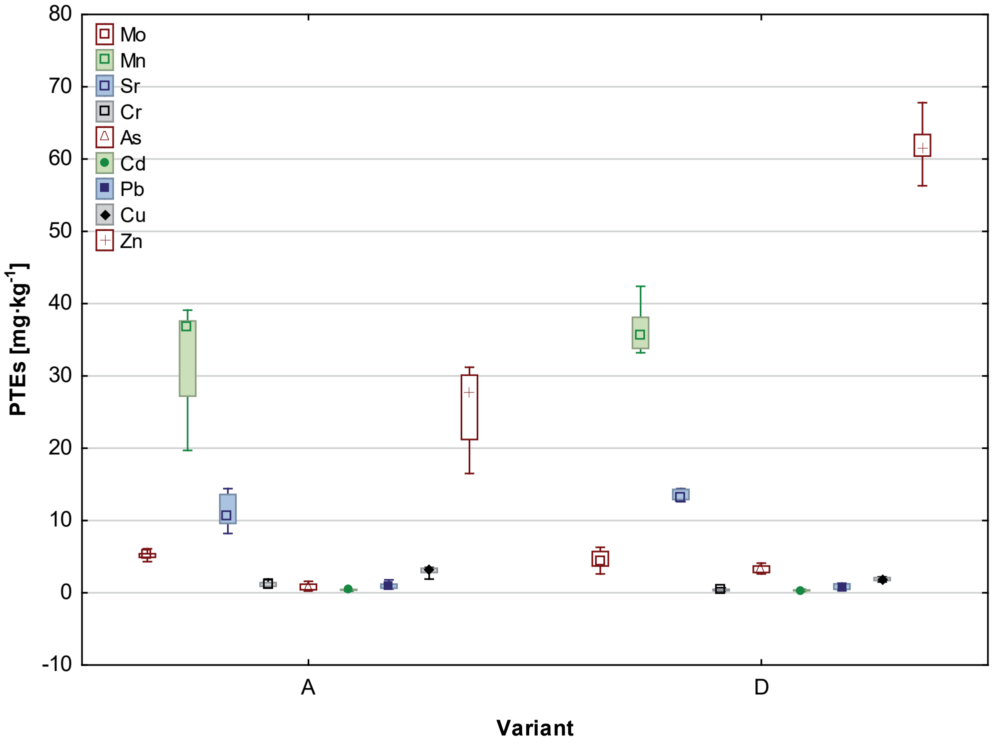

Fig. 3. Bioavailability of individual PTEs when comparing the variants A and D.

According to the study [21], no correlation was found between Mo in the soil and either Zn or Cu in the tested plant. However, the design of our experiments was different. In that work, correlations between element contents in soils of several soil types and in perennial grassland plants were investigated in two mountain areas. The interactions were influenced by a complex of factors that determine their basic conditions, such as different soil types, specific physical properties of the soil (especially grain size and abundance of clay fraction), contents of essential nutrients (P, K, Mg), and the presence of other microbiogenic elements as well. At the same time, it is possible to point out the different affinity of autochthonous plant species (species of grass-herbaceous community of semi-natural to natural ecosystems) and allochthonous cultivated cereal species, namely barley grown in our experiment.

Sr, which is generally considered an indicator of radioactive pollution, can also be included among the PTEs [22]. However, this element is also an additive in lignite coal, which was burned at the Nováky power plant from the 1960s to the end of the 1980s.

The issue of Sr in plants, as well as mobility in the soil–plant system, is dealt with by [23, 24], who point

Table 10. Parameters of the Mann-Whitney test for the comparison of the variants A and E.

PTEs	Sum of the ranks A	Sum of the ranks E	U-test	Adjusted Z	p-value	Level of significance
Mo	55	155	0	-3.74	0.000	***
Mn	116	94	39	0.79	0.427	–
Sr	55	155	0	-3.74	0.000	***
Cr	155	56	1	3.73	0.000	***
As	155	55	0	3.75	0.000	***
Cd	55	155	0	-3.75	0.000	***
Pb	147	64	9	3.10	0.002	**
Cu	146	65	10	3.04	0.002	**
Zn	55	155	0	-3.74	0.000	***

Level of significance p<0.05*, p<0.01**, p<0.001***.

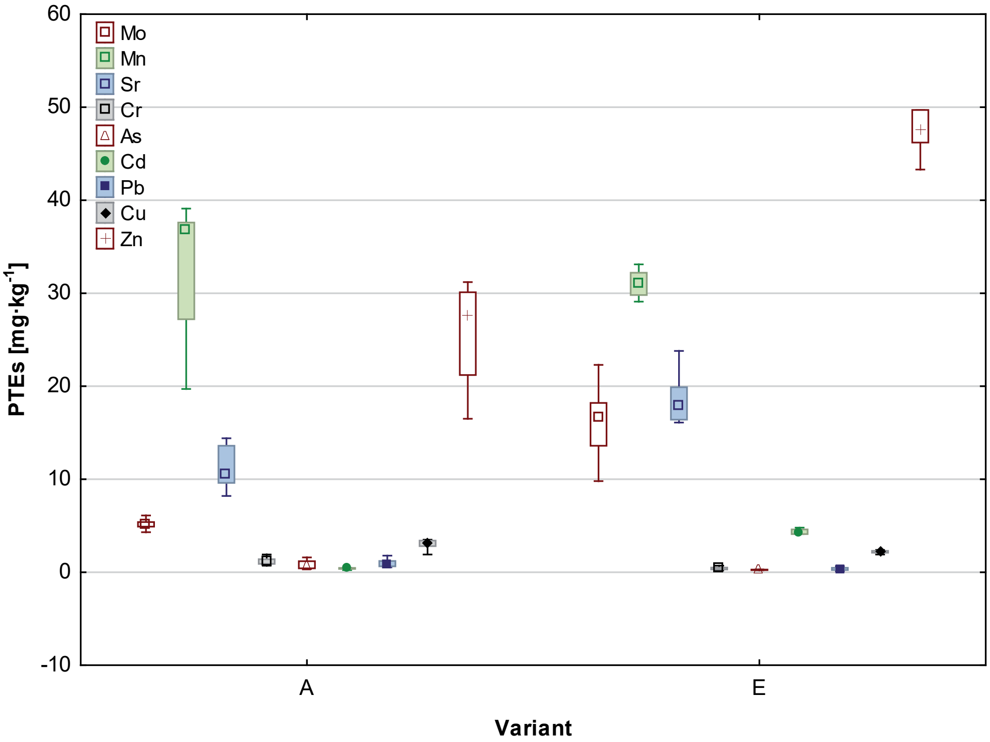

Fig. 4. Bioavailability of individual PTEs when comparing the variants A and E.

out, among other things, that the increased content of this element in the substrate was manifested not only by its excessive accumulation in the dry matter of barley, but also resulted in an increased intake of Mo and Zn into experimentally grown plants (increased concentration of these elements in the dry matter of barley). The positive correlation between Sr and Zn was also confirmed in the study [25]. However, no significant correlation was confirmed between Sr and Mo in the same study [25]. This study aimed to clarify the interactions between Cs, Sr, and other mineral elements. 33 different varieties were used from the plants of the genus *Amaranthus*, and the concentrations of 23 mineral elements in shoots grown in fields in Fukushima Prefecture were studied. The results of this study highlighted species differences in the intake of certain elements by plants of the genus *Amaranthus*. On the contrary, the addition of Sr antagonistically affected the intake of Cr, Cu, and As, which was reflected in a decrease in the concentration of these elements in the dry matter of barley straw. Regarding the evaluation of the Mo and Sr contents in separate variants of the experiment, the interaction of Mo-Sr elements (or also Mo-Sr-Zn elements) is obvious.

In their study, Chu et al. [25] did not find a correlation between the pairs Sr–Cr, Sr–Cu, or Sr–As, which may have been influenced by the aforementioned factors related to species and varietal differences in element uptake. In environmental chemistry, As is considered an element with a high degree of negative effects on living organisms, including plants. It often enters the environment from the combustion of poor-quality types of lignite coal, which, as above-mentioned, was also used in the power plant in Nováky. Therefore, it is perceived as a toxic element, or a PTEs. The increased content of this element in the substrate logically caused its excessive accumulation in the dry matter of the straw of experimentally grown barley. However, its increased intake into the plant organism also caused an increase in the concentration of Zn in the dry matter of the straw and, at the same time, a decrease in the concentrations of Cr and Cu.

A positive correlation between As and Zn was found in a study [26], in which 9 rice genotypes were studied. According to a study [27], a strongly positive correlation between As and Cr was observed in rice, which does not correspond with our results. The negative correlation between As and Cu was confirmed by a study [28]. This finding is consistent with our results. The variety of these results may indicate that when assessing the interaction of these elements, there are factors beyond their presence and content in the soil, including their uptake and correlation with the contents in the dry matter of plants, as well as other ecological and environmental factors that are important.

The results of Ngugi et al. [29] indicate the mobility of Cd, its uptake and accumulation in spinach, kale, and amaranth vegetables under silicon fertilization. The results from the greenhouse experiments, Onchoke and Fateru [30], lead to the conclusion on the role played by the biosolids in cleanup and remediation for Cd and Mn, which increased in plant parts with composted wastewater sludge compositions. The model of sorption of Cu, Zn, Cd, and Mn from sewage sludge, as well as their chemistry, was also discussed by Samešová et al. [31] and Ďuricová et al. [32].

These authors [30] also point out that toxic Cd tends to be sequestered in the roots vis-à-vis Mn, which is translocated to the leaves. The element Cd is likely to be distributed differently in plants. It is not distributed in the same way as, for example, Mn.

The results of the study by Hao et al. [33] are interesting. In this study, the effects of foliar application of fertilizers on spring wheat yield, Cd accumulation, and trace element contents were studied by applying three kinds of fertilizers (multi-element compound fertilizer, manganese-zinc micro fertilizer, and foliar silicon fertilizer) to spring wheat planted in mildly and moderately Cd-polluted areas. The results showed that the yield of wheat increased by 17.1%, 15.7%, and 16.9% when fertilized with a multi-element compound fertilizer, manganese-zinc micro fertilizer, and silicon fertilizer, respectively, compared with the control. In addition, all three foliar fertilizers reduced the Cd content in wheat grains to below the standard value of food pollutants (≤0.1mg·kg), and significantly reduced the transport of Cd from glume to grain, among which manganese-zinc micro fertilizer had the best effect, with a Cd reduction rate of 41.7%. At the same time, the manganese-zinc microfertilizer significantly increased the absorption of trace elements in wheat organs. These results indicate that the foliar application of manganese-zinc micro fertilizer could be an effective way to increase wheat yield, inhibit Cd accumulation, and increase nutrient absorption in mildly to moderately Cd-polluted areas.

In turn, the authors Rahman et al. [34] discussed the effect of exogenously applied Zn on the toxicity and accumulation of Cd in the annual sunflower (*Helianthus annuus* L.), stating that Cd-toxicity curtailed the root length, shoot length, leaf area, chlorophyll a/b ratio, 100-seed weight, and biological yield up to 32.03%, 27.03%, 26.1%, 31.33%, 34.46%, and 22.37%, respectively. Exogenous application of Zn significantly improved the Cd-induced losses and increased the root length (37.9%), shoot length (48.4%), leaf area (56.2%), chlorophyll a/b ratio (65.64%), 100-seed weight (66.98%), and biological yield (74.04%). Mineral ions, e.g., Na^+, of root and shoot (61.02% and 29.42%) increased under Cd stress, whereas K^+ and Ca^{2+} decreased due to Cd toxicity in both root and shoot. Generally, the application of Zn improved the polyphenolic compounds and ion contents of plants under stressed conditions. At the same time, the application of Zn (100 ppm level as compared to 50) substantially increased the flavonoid contents up to 92.92% as compared to anthocyanin contents of 52.11% in Cd-stressed plants. Current findings reveal that using Zn could be an effective strategy against abiotic stresses and could be suggested for the decontamination of mildly to moderately contaminated soils containing Cd.

Although the work of Onchoke and Fateru [30] and Hao et al. [33] points to the interaction between Cd and Mn, and between Cd and Zn, respectively, our results relating to spring barley only confirmed the interaction between Cd and Zn. The importance of the synergistic or antagonistic effects of these elements may also be influenced by the bioavailability of Si, and it should be noted that we added Cd to the soil substrate at an elevated level in our experiment, which may have influenced the conformational uptake of some elements.

The toxic effect of Cd on the growth, development, and photosynthesis process of pea (*Pisum sativum* L.) was confirmed by Orzoł et al. [35]. Root and shoot samples of pea were examined, and the accumulation of Cd, especially in the roots, was found, which proves the excludable properties of the plant. Recently, the effect of Cd on plants, specifically seedlings of the tea plant (*Camellia sinensis* L.), was investigated in a study [36], which reported an increased concentration of Cd in the root cells of this plant.

The influence of Cd, as well as other elements (As, Pb, Zn), on lettuce (*Lactuca sativa* var. *capitata*) under hydroponic conditions was investigated by Lhotská et al. [37]. The experiment focused only on the combined effect of selected toxic elements without the influence of soil, due to the hydroponic conditions. Pre-cultivated (stage of six true leaves) plants were grown in a control and contaminated hydroponic culture for 14 days. The mixture of toxic elements (As, Cd, Pb, and Zn) in the contaminated solution corresponded to the water-soluble fraction of the soil from the anthropogenically contaminated area of the river Litavka (Czech Republic). The reaction of the plants was measured by determining the content of toxic elements, dry biomass, and gas exchange parameters. Lettuce accumulates toxic elements mainly in the roots with low translocation into the leaves. The uptake of toxic elements harmed photosynthesis and caused a decrease in the rate of photosynthesis, the rate of transpiration, and the conductivity of the stomata. As a result, the total production of dry plant biomass decreased. The results show that contamination under hydroponic conditions had an irreversible effect on plant growth due to direct contact between the roots and contaminated solutions [30]. In our experiment, we added this element in a similar form to [36], i.e., $CdCl_2 \cdot 2\frac{1}{2}\ H_2O$, in order to present its representation in soils recorded at the end of the last century in the area of Horná Nitra.

To an increased extent, it did not get into the soil around the power plant in Nováky from the combustion process [36]. However, in the 1970s, an environmental accident occurred as a result of the rupture of a landfill dam containing burnt fly ash. To eliminate the potential negative effects of As, which was known to be part of fly ash in higher concentrations, uncontrolled amounts of superphosphate were applied to agricultural soils as part of remediation measures.

However, the superphosphates produced at that time contained a significant amount of ballast substances, including cadmium (Cd). It is paradoxical that the remediation of the environmental accident contributed to the intoxication of soil by Cd in the area near Nováky. As we model this state by experiment, we also focused on the assessment of the content of this element after its active addition to the dry matter of the grown barley straw. It follows from the results that its addition increased the content of Cd in the dry matter of experimentally grown plants (barley straw). However, the addition of Cd increased the concentration of Mo, Sr, and Zn, too.

Our results are consistent with those of Zhu et al. [38], in which a positive correlation between Cd and Zn was determined in the root, stem, leaf, and fruit of beans. A positive correlation between Cd and Zn was also confirmed by another research [39]. This finding contradicts the results of the study by Cheng et al., according to which no clear relationship was found between the concentrations of Cd and Zn in rice grains [26]. The technologies of rice cultivation (agrotechnical conditions), due to the modification of the hydric regime, are different from those of barley, but also of the above-mentioned crop, such as beans (*Phaseolus* sp. L.). Increased intake of Cd by plants caused a decrease in the accumulation of the already mentioned As, but also Cr, Pb, and Cu. This finding does not correspond with the findings of a study [39], in which a positive correlation between Cd and Cu was determined in the edible parts of crops. In the same study [39], the correlation between Cd and Pb was not confirmed in low-contaminated soil, but a positive correlation was confirmed in heavily contaminated soil. The study points out that, e.g., sesame seeds absorb metals more than pepper fruits, from which it is possible to deduce species differences in relation to the intake of PTEs, which may, to some extent, explain the differences among our results. The correlation was also not confirmed in the study [26]. Based on the results of the study [26], a positive correlation was found between Cd and As, which does not correspond with our results. In agriculture, straw is considered a by-product. Unlike grain, it is not used directly for food, but it can be partly used in feeding livestock, or even more often, it is used as bedding (for cattle or sheep). Recently, straw has also been used as a biofuel. This simple calculation suggests that if increased amounts of PTEs accumulate in the straw, there is not only a risk of penetration into the trophic chain, but also the risk of reverse contamination of the environment within the biogeochemical cycle of substrate – soil – water – plant.

As mentioned above, there are not many studies that examine the combined influence of PTEs. This fact is also pointed out by [40], who present the results of studies on the influence of selected concentrations (10-100 $mg \cdot dm^{-3}$) of heavy metals (Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Zn) and metalloids (As, Sb, Se) on the germination and root elongation of cress *(Lepidium sativum* L). There are not many studies on the phytotoxicity of heavy metals and metalloids with the complex use of single plant species so far. Based on the germination index (GI) and inhibition concentration IC_{50}, the following order of phytotoxicity of the tested elements was determined: Se> As> Hg> Sb >Mo > Cd> Co > Zn > Ni.

Conclusions

In many cases, positive or negative correlation was found between the bioavailability of metals in different variants of contamination. Mo, Sr, As, or Cd at increased concentrations in the soil had a positive effect on the intake of Zn into barley straw. For PTEs, Mo, Sr, and Cd confirmed As as a blocker of intake. The only confirmed correlation with Pb was found when decreasing its contamination by Cd in soil. Of all the variants of contamination, it was Cd that supported the highest intake of the elements.

It led to an increase in the uptake of Mo, Sr, Cd, and Zn. On the other hand, the same element acted as a blocker of the largest number of PTEs compared to the other contaminants, namely Cr, As, Pb, and Cu. The results of our study did not always correspond with the results of the discussed research studies. This discrepancy could be caused by different cultivation technologies of the studied crops, deviations in the research conditions, or species and varietal differences in the intake of PTEs.

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Conflict of Interest

The authors declare no conflict of interest.

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