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Effect of adding furnace ash from bituminous coal combustion to soil on phytoavailability of selected metals

The research on the effect of furnace ash from bituminous coal combustion on the uptake of Cr, Cu, Ni, Fe, Mn, Al by maize (*Zea mays* L.) was conducted under conditions of a three-year pot experiment. The arable soil in the pot experiment was amended with furnace ash in the amount of 23.33 g·pot^{-1} (corresponding to 20 t·ha^{-1}) and with increasing doses of cadmium (3÷15 mg·kg^{-1} soil DM). Application of ash and cadmium in the amount of 3÷5 mg·kg^{-1} DM to the soil had a significant effect on the increase in the yield of above-ground parts and roots of maize. Application of subsequent doses of cadmium (7.5÷15 mg·kg^{-1}) caused a considerable reduction in the yield of the tested plant. The research shows that the applied furnace ash reduced the depression in yielding of maize. Introduction of furnace ash to cadmium-contaminated soil caused an increase in the content of Cr, Fe, Ni, Cu and Al in maize biomass and a decrease in the content of Mn in maize. Among the studied metals, Mn was translocated from roots to above-ground parts the most efficiently, and Al - the least efficiently, evidence of which are the highest values of the translocation factor for Mn, and the lowest values for Al. The research showed that ash introduced to cadmium-contaminated soil did not immobilize the above-mentioned metals, and thereby did not reduce the phytoavailability. In general, contamination of the soil with cadmium and introduction of ash stimulated uptake of the metals by maize. We observed that roots took up more Cr, Fe, Ni and Al, whereas above-ground parts of maize took up more Mn and Cu. The lowest uptake of the studied metals by maize was observed in the treatment where only furnace ash was applied.

Keywords: **ash, Cr, Mn, Fe, Ni, Cu, Al, maize, tolerance index, metal translocation factor, metal content and uptake**

Introduction

Being a product of bituminous coal combustion, furnace ash constitutes an economic and environmental problem due to the content of toxic metals and other substances. Numerous attempts are currently being made to utilize bituminous coal fly ash also as a raw material for production of zeolites and other metal-binding materials [1-3]. Other studies show that furnace ash obtained from combustion of bituminous coal has unfavorable physical and chemical properties; hence it is difficult to use it in agriculture to fertilize cultivated plants [4]. Moreover, legal acts issued by the Ministry of Agriculture and Rural Development do not permit application of furnace ash from bituminous coal combustion to arable soils [5, 6]. However, furnace ash constitutes a potential source of valuable microelements and macroelements; hence it can be used in biological reclamation of landfills [7-9]. Some researchers report that, after application to soil, furnace ash derived from combustion of bituminous coal improves its physical and chemical properties [10]. In Poland, it is permitted to use furnace ash from bituminous coal combustion in reclamation of landfills, including creation of reclamation layer [11]. After application of furnace ash from bituminous coal combustion to the soil environment, availability of heavy metals from this waste may increase. The high concentration of heavy metals in furnace ash results from a considerable mass loss during carbon combustion and low mobility of these elements [12]. That is why furnace ash, on account of its specific physical and chemical properties, can bind heavy metals or release them into the environment [13, 14]. The aim of the research was to determine the effect of the percentage of furnace ash derived from combustion of bituminous coal as well as of increasing doses of cadmium applied to soil on the yielding and uptake of Cr, Mn, Fe, Ni, Cu, Al by maize.

1. Material and research methods

The research on the effect of furnace ash on the yielding and uptake of Cr, Cu, Ni, Fe, Mn and Al by maize (*Zea mays* L.), "KOKA" cultivar, was conducted under conditions of a three-year pot experiment.

1.1. Soil, furnace ash

Arable soil collected from the humus horizon was used in the strict pot experiment. Sand soils contained 95% sand, 2% dust, 3% floatable particles [15]. The soil used in the experiment had neutral reaction (Tab. 1). The soil came from the Bukowno commune, a region impacted by the Boleslaw Mine and Metallurgical Plant, which processes zinc and lead ores. The soil had a natural (0^o) content of Cr, Cu, Ni, and an elevated (I^o) content of Pb, was weakly (II^o) contaminated with Zn, and moderately (III^o) contaminated with Cd (Tab. 1), [16].

Furnace ash derived from combustion of bituminous coal, i.e. a dust-slag compound from wet treatment of furnace waste (catalogue number 100180), was used in the experiment [17]. Determination of the granulometric composition of furnace ash was performed according to methodology recommended for arable soils [15]. The grain size analysis showed that, in terms of granulometric composition, the studied furnace ash corresponded to sandy loam (Tab. 1). Furnace ash, whose chemical composition is provided in Table 1, was collected from the furnace waste landfill in Oświęcim. Heavy metal content (Cr, Zn, Pb, Cu, Cd, Ni) in the furnace ash was significantly lower than provided in the Ordinance of the Ministry of Environment on soil and earth quality standards [18].

Table 1. **Physicochemical characteristics of soil and ash used in the experiment**

Parameter	Unit	Soil	Ash	IUNG* scale	Permissible**
$pH_{(KCl)}$	-	7.06	9.85	-	-
$pH_{(H2O)}$	-	7.33	10.06	-	-
Texture	-	Sand soil	Sandy silty loam silt	-	-
Cr	$mg \cdot kg^{-1}$ DM	5.48	33.85	0	150
Zn		251.25	93.75	II	300
Pb		45.10	18.65	I	100
Cu		6.00	74.50	0	150
Cd		2.75	0.28	III	4
Ni		3.38	39.98	0	100
Fe		710.0	39950.0	-	-
Mn		153.25	857.5	-	-
Al		962.5	13775.0	-	-

*0 - natural content, I - elevated content, II - slight content, III - medium content,
**Permissible content according to ME Regulation [17]

1.2. Scheme of the experiment

The experiment was comprised of 9 treatments which differed in the addition of ash and cadmium (Tab. 2). Treatment 1 (control) consisted of soil only, treatment 2 consisted of soil with ash amendment, in treatments 3-8 soil mixed with ash was amended with increasing amounts of cadmium (3.0 to 15.0 $mg \cdot kg^{-1}$ DM), treatment 9 consisted of furnace ash only. Furnace ash in the amount of 23.33 $g \cdot pot^{-1}$, which corresponded to 20 t $DM \cdot ha^{-1}$, was added to soil in treatments 2-8. The experiment was conducted in four replications, in 3.5 kg polyethylene pots. In the first year of the experiment, the soil was amended once with cadmium in the form of aqueous solution of $3CdSO_4 \cdot 8H_2O$. Cadmium is a metal that is chemically quite active, and cadmium sulfate solution is bioavailable and toxic for plants [19, 20].

1.3. Conditions of the experiment

In all treatments, fixed NPK fertilization was applied annually in the following amounts: 0.3 mg N, 0.08 mg P, 0.2 K $mg \cdot kg^{-1}$ soil DM, in the form of NH_4NO_3, KH_2PO_4, KCl. Mineral fertilizers in the form of aquatic solutions were used every year, one week prior to plant sowing, and mixed thoroughly with the soil. Vegetation period for maize was, on average, 115 days. During vegetation, the plants were watered with redistilled water, so that the soil moisture was maintained at 60% of the maximum water capacity. Above-ground parts and roots of maize were collected each year from each pot, and then, after drying in a dryer at 105°C, the amount of yield of the absolutely dry matter was determined and expressed in g $DM \cdot pot^{-1}$.

1.4. Determinations, calculations and statistical analysis of the results

Cr, Cu, Ni, Fe, Mn and Al were determined in the plant material from each repetition after dry mineralization, using the ICP-OES method. This presents the content of the above-mentioned metals in above-ground parts and roots of maize as a weighted mean from three years of research (Figs. 1, 2).

Annual uptake of metals (P) was calculated as the product of dry matter yield (A) and the nutrient content (X), according to the formula: $P = A \cdot X$. The uptake of metals by above-ground parts and roots of maize is presented as the sum from three years of research (Figs. 3, 4). Tolerance index was calculated as a ratio of the yield obtained on contaminated soil to the yield obtained in the control treatment (Tab. 2). The metal translocation factor was calculated as a ratio of the content of the metal in above-ground parts to its content in roots (Tab. 3). Microsoft Excel 7.0 spreadsheet was used for statistical calculations. Significance of differences between the compared means of yield of maize, content and uptake of metals were determined using the Duncan method. Analysis of variance and Duncan's test were carried out at a significance level of $\alpha \leq 0.01$. For selected parameters, the value of the Pearson linear correlation index (r) was computed at a significance level of $p < 0.01$.

2. Research results

2.1. Yield of plants

Crop yielding is an important indicator of plant reaction to environmental conditions. The yield of above-ground parts and roots of maize that was obtained in the experiment was varied and depended on pollution, the level of soil contamination with cadmium and on the year of the research (Tab. 2). In the experiment, a higher yield of above-ground parts than of roots was observed. Depending on treatment and year of the research, the amount of yield of above-ground parts varied from 13.08 to 43.02 g DM, and in the case of roots - from 2.79 to 10.60 $g \cdot pot^{-1}$ (Tab. 2).

The highest yield of maize was obtained on soil with ash amendment (treatment 2), and the lowest in the treatment where only ash was applied (treatment 9). Difference in yielding between these treatments reached over 29.94 $g\ DM \cdot pot^{-1}$ for above-ground parts, and 7.81 $g\ DM \cdot pot^{-1}$ in the case of roots. The research shows that the addition of ash to light soil (treatment 2) contributed to a significant increase in the amount of yield of above-ground parts of roots of maize. The increase in yield of above-ground parts in subsequent years of the research reached, respectively, over 7, 7, and 22%, and the increase in yield of maize roots was even higher and reached, respectively, over: 18, 19, 25% in relation to the control. The analysis of yield of treatments 1 and 2 (Tab. 2) shows that introduction of ash to the soil, regardless of the analyzed part of the tested plant or the year of the experiment, contributed to an increase in yield. Soil contamination with cadmium from 3.0 to 5.0 $mg \cdot kg^{-1}$ soil DM (treatments 3-5) did not have a significant effect on maize yield. This stability of maize yielding in the above-mentioned treatments may be explained by, among other things, a positive effect of ash on physicochemical properties of the light soil used in the experiment, a change in soil reaction, and also by a reduction in cadmium bioavailability (3rd degree of soil contamination with cadmium, 2nd degree of soil contamination with zinc, 1st degree of soil contamination with lead).

Table 2. **Yield and tolerance index**

Number of treatment*	Doses Cd/Ash	Yield, g DM·pot^{-1}			Tolerance index (TI)**		
		1st***	2nd	3rd	1st	2nd	3rd
		Above-ground parts			Above-ground parts		
1	Control	33.12	38.65	34.99	-	-	-
2	0 + A	35.69	41.37	43.02	1.08	1.07	1.23
3	3 + A	35.34	41.26	42.09	1.07	1.07	1.20
4	4 + A	35.44	41.71	42.87	1.07	1.08	1.23
5	5 + A	34.44	39.92	41.82	1.04	1.03	1.20
6	7.5 + A	31.03	36.46	38.26	0.94	0.94	1.09
7	10 + A	29.97	35.53	36.30	0.90	0.92	1.04
8	15 + A	24.51	30.07	29.93	0.74	0.78	0.86
9	A	13.08	18.31	17.12	0.39	0.47	0.49
LSD $\alpha \leq 0.01$		2.53	2.76	7.54		-	-
		Roots			Roots		
1	Control	7.05	8.14	8.46	-	-	-
2	0 + A	8.34	9.73	10.60	1.18	1.20	1.25
3	3 + A	7.73	8.70	9.42	1.10	1.07	1.11
4	4 + A	8.25	8.68	9.71	1.17	1.07	1.15
5	5 + A	7.85	8.56	9.00	1.11	1.05	1.06
6	7.5 + A	6.97	7.80	8.25	0.99	0.96	0.98
7	10 + A	6.32	7.14	7.80	0.90	0.88	0.92
8	15 + A	5.61	6.87	6.80	0.80	0.84	0.80
9	A	2.79	3.86	3.69	0.40	0.47	0.44
LSD $\alpha \leq 0.01$		1.14	1.05	1.26	-	-	-

*Treatments: 1 - Control; 2 - Soil + Ash; 3 - 3 mg Cd + Ash; 4 - 4 mg Cd + Ash; 5 - 5 mg Cd + Ash; 6 - 7,5 mg Cd + Ash; 7 - 10 mg Cd + Ash; 8 - 15 mg Cd + Ash; 9 - Only Ash
**TI - Tolerance index which was estimated as the ratio of the yield obtained in polluted objects (treatments 2-9) and the yield generated in the control (treatment 1)
***Years

The increase in soil contamination with cadmium from 7.5 to 10 mg·kg^{-1} soil DM (treatments 6-7) led to depression in yielding of maize, although it was not statistically significant. The highest cadmium dose applied to the soil in the amount of 15 mg·kg^{-1} soil DM (treatment 8) caused a significant decrease in maize yield. In subsequent years of the research, the decrease in yield of above-ground parts was, respectively, over 25, 22, 14%, and in the case of roots - 20, 15, 19% in relation to the control. Application of only furnace ash (treatment 9) had a significant effect on the decrease in yield of above-ground parts and roots of maize, which in subsequent years of vegetation was, respectively, over: 60, 52, 51% in relation to the control. Attention is drawn to the fact that higher yield of maize was observed in the third year after application of cadmium and ash to the soil, which can be explained by improvement of physicochemical properties of the soil, a reduction in cadmium solubility, and thereby a reduction in phytoavailability of this metal.

2.2. Tolerance index

Maize sensitivity to the presence of cadmium and furnace ash in the soil was determined based on tolerance index. In recent years, tolerance index (TI) has been regarded as the most reliable indicator for determining compounds which are toxic for plants in soils [21, 22]. Tolerance index may assume values TI < 1, TI = 1, T > 1. If this index is less than one, it implies growth inhibition of plants, and sometimes their total death. If the index equals one, it is indicative of no effect of contamination on yielding. In the event when this index is more than one, this informs us about a positive effect of contamination on the growth and development of plants.

The tolerance index calculated for maize assumed values over 1 in treatments 2-5, where ash and cadmium were amended to soil in doses of 3÷5 $mg \cdot kg^{-1}$ soil DM (Tab. 2). Value of the index below 1 was obtained in the treatments where cadmium was added in doses of 7.5÷15 $mg \cdot kg^{-1}$ DM, and the lowest TI value was obtained in the treatment amended only with furnace ash (treatment 9). The presented research shows that TI value obtained in treatments 6-8 was determined by cadmium dose and percentage of ash (treatment 9).

The conducted analysis of yielding indices (the amount of yield, tolerance index) suggests that, compared with the control treatment, furnace ash that had been added to the soil contaminated with heavy metals (treatments 2-5) had improved yielding. It has been shown that furnace ash introduced to the cadmium-contaminated soil alleviated the effects of soil contamination with heavy metals on the amount of yield.

2.3. Content of Cr, Cu, Ni, Fe, Mn and Al in maize

Special attention was paid in the conducted research to such metals as: Cr, Mn, Fe, Ni, Cu, Al. Selection of these metals was justifiable owing to ash contamination with these elements; the content of these elements in the ash was, respectively, 6-, 6-, 56-, 11-, 12-, 14-fold higher than in the soil (Tab. 1). The following were assumed as indicators of cadmium interaction with the studied metals: content, translocation and uptake of the metals by maize.

Soil reaction is of great importance in the uptake of metals by plants, that is why the pH of the environment should be taken into account. Implementation of cadmium salt and furnace ash to the soil changed its reaction, which had an effect on the uptake of heavy metals by maize. After the experiment, the control soil still had neutral reaction (pH_{KCl} = 6.94), whereas reaction of the soil that was contaminated with cadmium and fertilized with ash (treatments 2-8) was slightly lower and varied from 6.98 to 6.79. Furnace ash alone (treatment 9) still had alkaline reaction, the $pH_{(KCl)}$ value was more than 9.70 (Tab. 3).

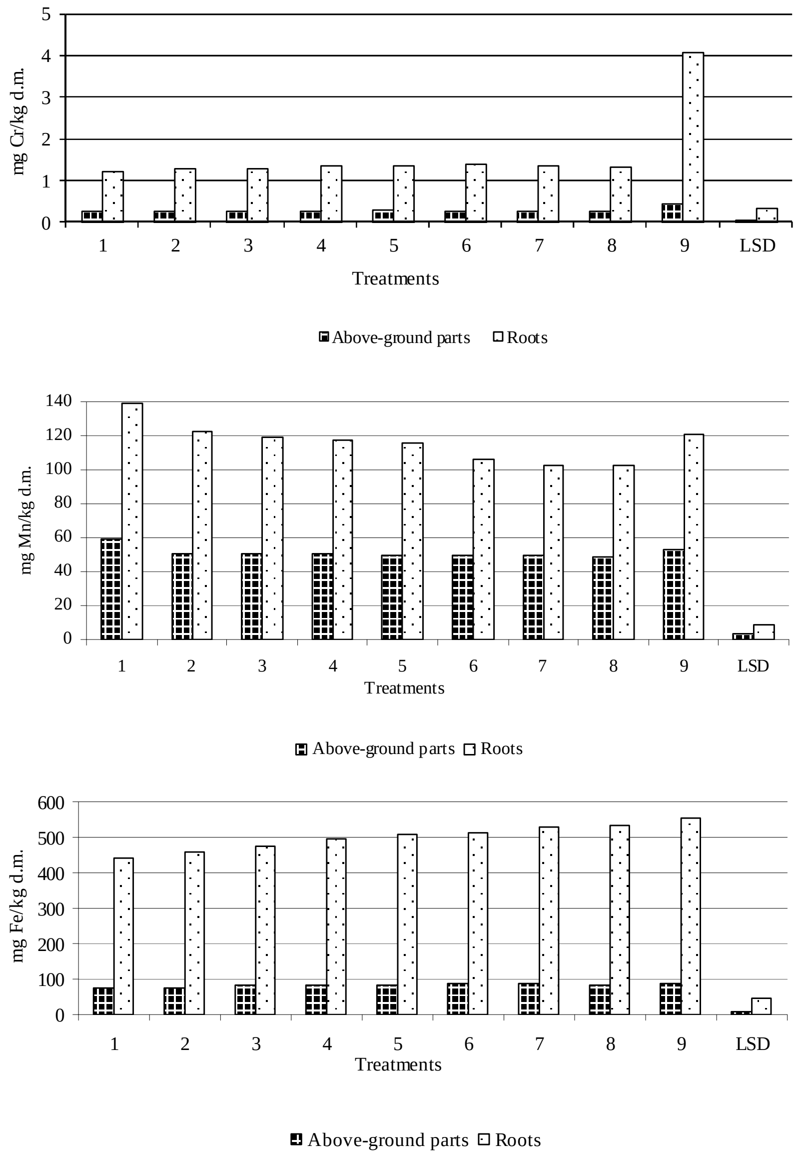

Fig. 1. Content of Cr, Mn and Fe in maize

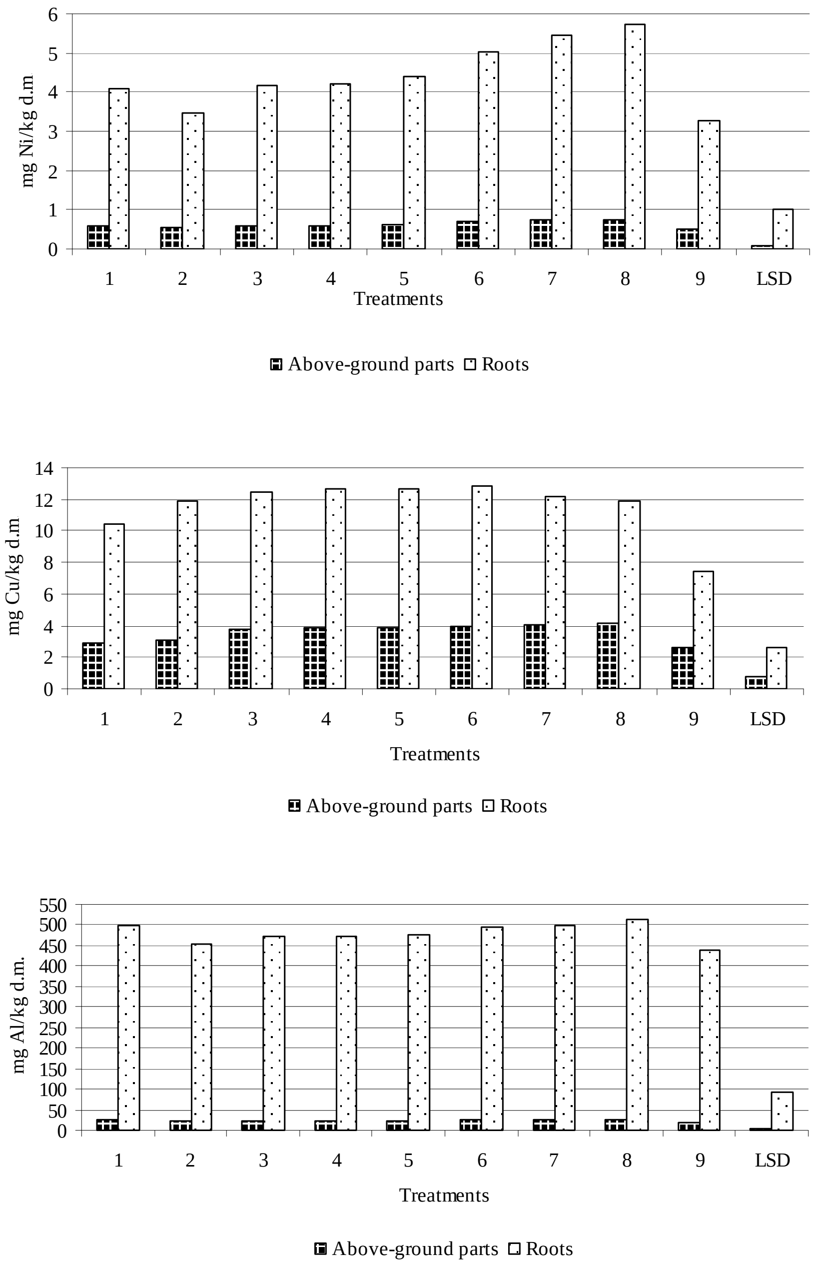

Fig. 2. Content of Ni, Cu and Al in maize

The lowest content of Cr and Fe was found in above-ground parts and in roots of maize from the control treatment, and the highest from treatment 9 where the substratum consisted of ash only (Fig. 1). In the case of nickel, copper and aluminum (Ni, Cu and Al), the lowest content of these elements was determined in plants obtained from the treatment amended only with furnace ash (treatment 9), (Fig. 2). Introduction of furnace ash to the soil as well as increasing cadmium doses led to a systematic increase in the content of Cr, Ni, Cu, Fe and Al in maize (treatments 3-8). The research shows that introduction of cadmium (in the amount of $3 \div 15$ mg·kg^{-1} DM) to the soil fertilized with furnace ash increases the content of these metals in the index parts of maize.

In the case of Mn, where the content of this metal in the furnace ash was more than 5 times higher than in the soil; an inverse relationship was determined. That is to say, the highest content of Mn was determined in maize cultivated on arable soil (control, treatment 1). Introduction of both furnace ash and increasing doses of cadmium to the soil (in the amount of $3 \div 15$ mg·kg DM) significantly decreased manganese content in above-ground parts and in roots of maize.

Linear correlation coefficients which describe the relationship between the dose of cadmium introduced to the soil, fertilized with ash and the content of metals in maize point to very strong relationships between selected metals. Strong correlations between the dose of cadmium introduced to the soil and the content of Mn, Ni and Cu in above-ground parts and roots of maize were shown. The research shows that introduction of cadmium to the soil fertilized with furnace ash was negatively correlated with Mn content in above-ground parts and roots of maize ($r = 0.611897 \div 0.812791$), and positively correlated with Ni content in above-ground parts and roots of maize ($r = 0.812979 \div 0.800625$). A slightly weaker relationship between cadmium dose in the soil and Cu content in above-ground parts of maize was observed ($r = 0.572205$). The research revealed that reaction of the soil into which cadmium and furnace ash were introduced was positively correlated with Cr content in above-ground parts and roots of maize ($r = 0.917007 \div 0.981489$). It was also shown that after the pot experiment soil reaction was negatively correlated with the content of Ni, Cu and Al in maize ($r = -0.736121 \div 0.490411$).

2.4. Metal translocation factor (TF)

Mobility of the studied metals in a plant was determined using the translocation factor (TF). This parameter represents the ratio of the content of the metal in the above-ground parts to its content in roots [23]. Relationships between the content of Cr, Mn, Fe, Ni, Cu and Al in above-ground parts and roots are presented in Table 3. A higher accumulation of metals in maize roots in relation to above-ground parts is confirmed by low values of translocation factor (TF) of the element (Tab. 3). Among the studied metals, Mn moved from roots to above-ground parts to the greatest degree, the evidence of which is the highest value of translocation factor. Based on the value of translocation factor (TF), metal mobility in maize was arranged in the following order of mobility: Mn < Cu < Cr < Fe < Ni < Al. The research shows that Al had the lowest mobility in the plant, which means that this element is accumulated mainly in roots.

Table 3. **Translocation factor of metals in the plant (TF)**

Number of treatment*	Doses Cd/Ash	pH_{KCl} soil	TF**					
			Cr	Mn	Fe	Ni	Cu	Al
1	Control	6.94	0.21	0.42	0.17	0.15	0.27	0.05
2	0 + A	6.98	0.21	0.41	0.16	0.16	0.26	0.05
3	3 + A	6.98	0.21	0.43	0.17	0.14	0.31	0.05
4	4 + A	6.93	0.20	0.43	0.17	0.14	0.31	0.05
5	5 + A	6.91	0.21	0.43	0.16	0.14	0.31	0.05
6	7.5 + A	6.86	0.20	0.47	0.17	0.14	0.31	0.05
7	10 + A	6.85	0.20	0.48	0.16	0.14	0.33	0.05
8	15 + A	6.79	0.20	0.47	0.16	0.13	0.35	0.05
9	A	9.70	0.11	0.44	0.16	0.15	0.36	0.04
Mean		7.21	0.19	0.44	0.17	0.14	0.31	0.05
Variation coefficient, %		12.95	16.95	5.62	2.85	6.26	10.01	5.30
LSD $\alpha \leq 0.01$		0.105	0.057	0.043	0.023	0.039	0.082	0.012

*Treatments: 1 - control; 2 - Soil + Ash; 3 - 3 mg Cd + Ash; 4 - 4 mg Cd + Ash; 5 - 5 mg Cd + Ash; 6 - 7.5 mg Cd + Ash; 7 - 10 mg Cd + Ash; 8 - 15 mg Cd + Ash; 9 - Only ash

**Translocation factor of metal calculated as the quotient of the metal content of the aerial parts to the content in the roots

The addition of ash to the cadmium contaminated soil (treatments 3-5) slightly decreased the values of the translocation factor for Cr, Fe, Ni. When analyzing the values of this factor, it is difficult to find a significant relationship between cadmium level and the content of the above-mentioned metals in maize.

Translocation factor (TF) stability for aluminum can be found interesting. Application of cadmium in the amounts from 3 to 15 mg $Cd \cdot kg^{-1}$ soil DM did not affect the relationships between the content in roots and above-ground parts of maize, and remained at the same level.

When only furnace ash was applied (treatment 9), it significantly decreased the value of translocation factor for Cr, Fe, Al. The value of translocation factor (TF) in that treatment was lowest, which may also point out to a defense mechanism in the root system of this plant.

Significant relationships between the content of Cr, Mn, Fe, Ni, Cu and Al in maize and the translocation factor were determined in the research. The value of correlation coefficient was negative and reached –0.841413 for Cr, –0.754085 for Mn, –0.574379 for Fe, –0.710882 for Ni, –0.468474 for Cu, –0.652618 for Al. This research shows that the content of metals in the plant was strongly associated with the ratio of the content of these metals in above-ground parts to their content in roots. Increasing cadmium doses in the soil were also significantly correlated with the translocation factor only for Mn ($r = 0.624476$).

2.5. Uptake of Cr, Mn, Fe, Ni, Cu and Al by maize

The uptake of metals by maize depended on the amount of yield, level of soil contamination with cadmium (treatment), and on the index part of the plant (Figs.

3, 4). It was established that above-ground parts of maize took up more Mn and Cu than roots. Higher uptake of these metals by above-ground parts of maize was associated with a four times higher yield of this part of plant compared with roots (Tab. 1). In the case of Cr, Fe, Ni and Al an inverse relationship was determined. Maize roots took up more of these metals than above-ground parts. The higher uptake of Cr, Fe, Ni and Al by roots can be explained by the fact that the content of these metals in roots was several times higher than in above-ground parts (Figs. 3, 4).

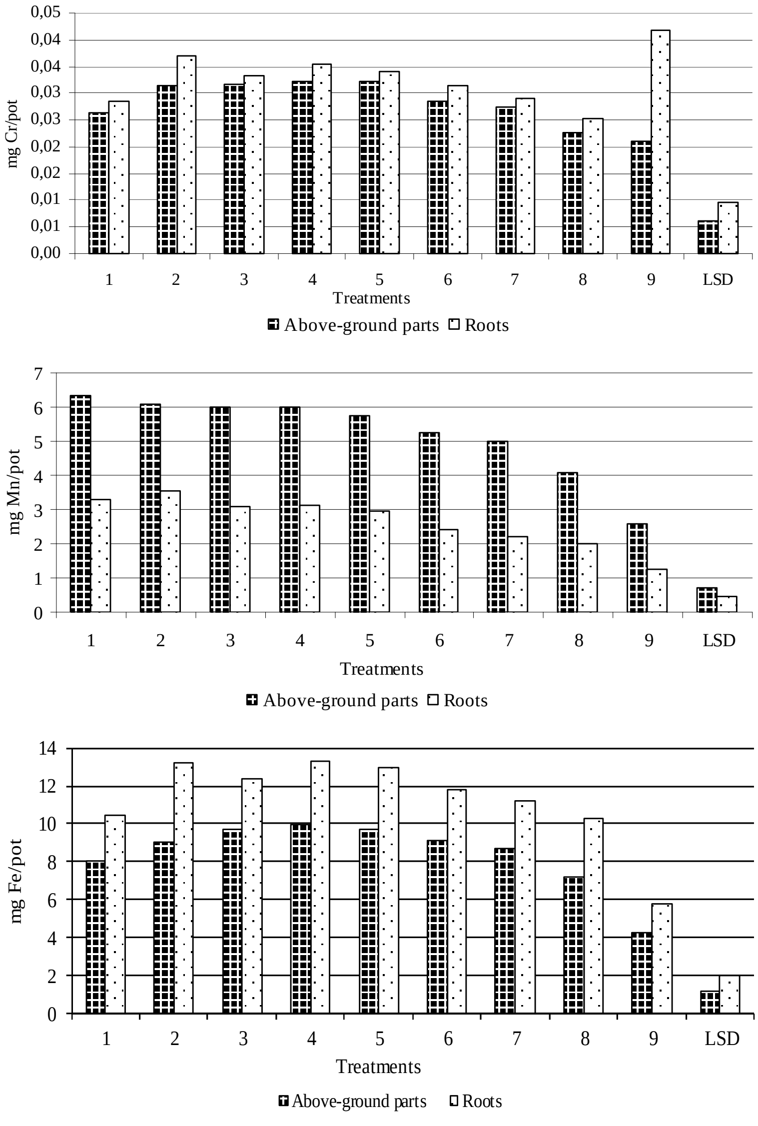

Fig. 3. Uptake of Cr, Mn and Fe by maize

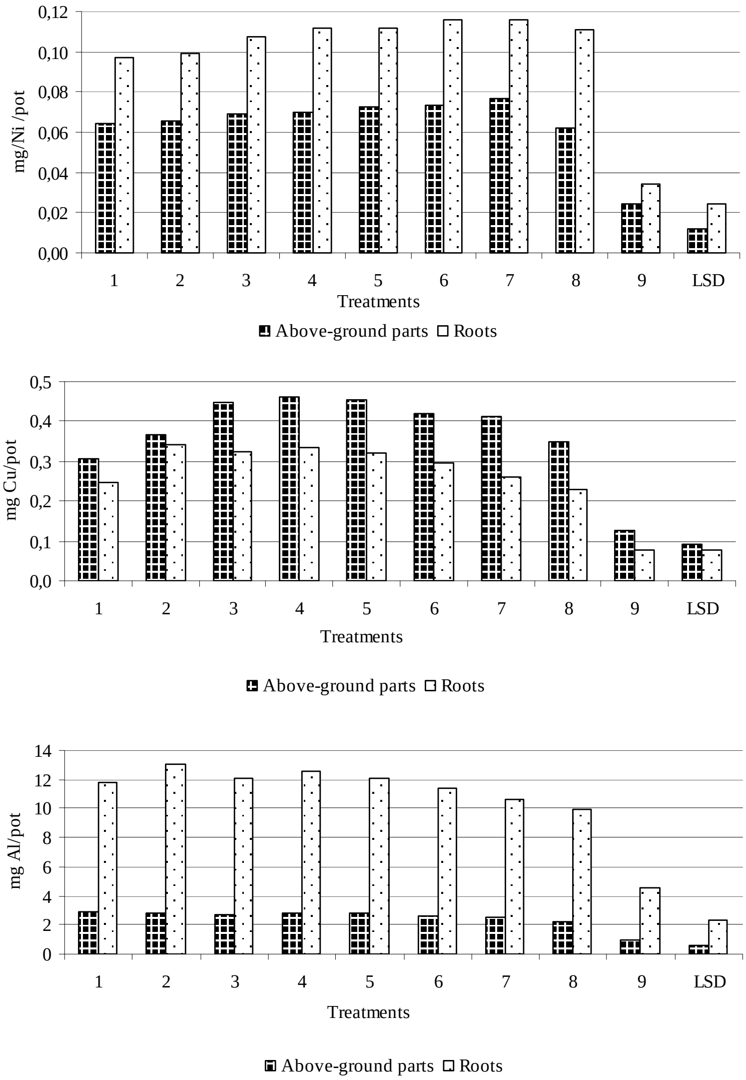

Fig. 4. Uptake of Ni, Cu and Al by maize

It was established that addition of cadmium in the amount from 3 to 10 mg Cd·kg^{-1} soil DM (treatments 3-7) did not have a significant effect on the amount of the studied metals being uptaken by maize. Only the highest dose of cadmium, i.e. 15 mg·kg^{-1} DM, significantly decreased the uptake of Cr, Mn, Fe and Al by above-ground parts of maize. A similar relationship was observed in the case of maize roots, where the decrease in the uptake of Cr, Mn, Fe and Al was determined at the highest level of soil contamination with cadmium (treatment 8).

Regardless of the analyzed index part of the plant, the highest uptake of Cr was determined in the treatment amended only with ash (treatment 9); Mn – in the control treatment; Fe and Al – in the treatment amended with ash (treatment 2); Ni – in the treatment amended with Cd in the amount of 10 $mg \cdot kg^{-1}$DM (treatment 7); Cu – in the treatment amended with Cd in the amount of 4 $mg \cdot kg^{-1}$ DM (treatment 4).

This research shows that introduction of cadmium to the soil fertilized with furnace ash was negatively correlated with the uptake of Cr ($r = -0.500461$) and positively correlated with the uptake of Ni ($r = 0.485683$) by maize roots. Strict interdependencies between the content of metals in above-ground parts and roots of maize and their uptake by these parts of the tested plant were also observed. The research revealed that reaction of the soil contaminated with cadmium and fertilized with furnace ash was negatively correlated with the uptake of Mn, Fe, Ni, Cu and Al by above-ground parts and roots of maize ($r = -0.756983 \div 0.895696$). In the case of Cr, a negative correlation between the reaction of the substratum and the uptake of this element by maize above-ground parts was determined, whereas the uptake of Cr by maize roots was positively correlated with the reaction of the substratum.

3. Discussion

Addition of furnace ash derived from combustion of bituminous coal to arable soil changes the chemical composition of plants. This has a substantial effect on the quality of biomass yield and is important in choosing the method of biomass management and in reclamation processes [24, 25].

The obtained results of our research confirm that the studied furnace ash improves crop yielding, and also has an effect on the change in the chemical composition of plants [7, 8, 10].

The research shows that when only furnace ash was applied (treatment 9), it did not constitute a potential source Ni, Mn, Cu and Al for maize, which may indicate that metals occurring in the studied waste have a low bioavailability for plants [12, 26]. Studies carried out by other authors [27, 28] indicate that Mn, Al, Ni, Cu and other metals occur in silicate and carbonate compounds which are difficult to dissolve in the soil solution. Moreover, introduction of ash to soil changes the reaction, which in consequence may have a significant effect on availability of these metals for plants. It was observed in the experiment that Mn content in the furnace ash was nearly 6 times higher than in the soil. It was established that introduction of cadmium to the soil fertilized with furnace ash decreased Mn content in the plants. The decrease in Mn content in maize resulted primarily from the low bioavailability of this element for the plants. This element occurs in poorly mobile forms, i.e. in carbonates, siderite, and ankerite [29].

According to the act on fertilizers and fertilization [30], furnace ash derived from combustion of bituminous coal cannot be used in agriculture, for fertilization of cultivated plants or for adjusting the reaction. It is permitted to use this type of waste in reclamation of landfills which may contain potentially high amounts of heavy metals [11]. That is why furnace ash, as mineral waste with alkaline reaction, can bind heavy metals in carbonate forms, not available for plants used in reclamation [10, 27].

The analysis of the obtained results indicates that introduction of cadmium to the soil fertilized with furnace ash increased the content of Cr, Ni, Cu, Fe, Al in the index parts of maize. This is probably connected with lowering of defense mechanisms of the plant under the influence of a toxic dose of cadmium [31]. Cadmium is a toxic element which disturbs the ionic equilibrium in the environment, destroys protein structures of plant organs, leads to uncontrolled uptake of metals by plants, which reduces plant quality [32].

Studies carried out by other authors [33] confirm that maize roots accumulate higher amounts of metals compared with above-ground parts. Plant roots limit the translocation of metals to above-ground parts, often through precipitation of these metals in cell organelles or by accumulating these metals in cell walls, on the basis of compartmentalization [34, 35].

In earlier research it was also determined that furnace ash influences the decrease in the value of translocation factor, which is surely connected with the alkalizing effect of the substratum [7, 8]. With alkaline reaction of the substratum, heavy metal uptake is limited, and the translocation of metals from roots to above-ground parts is hindered in these conditions. Moreover, availability of metals for plants depends on numerous physicochemical properties of the substratum, of the plant species [28, 36, 37]. According to Korzeniowska and Stanisławska-Glubiak [38], metal translocation factor (TF) can be strongly connected with the content of metals in a plant and with other plant parameters, including yielding. It was shown that, among the studied elements, aluminum was the least mobile. It resulted from the fact that, among other things, this element occurs in minerals of the oxide group (spinels), Al-Mg, insoluble in the soil solution [39].

Our research showed that the presence of ash in cadmium contaminated soil reduces the uptake of only Mn by above-ground parts and roots of maize. Only the highest dose of cadmium, i.e. 15 $mg \cdot kg^{-1}$ DM, significantly decreased the uptake of Cr, Mn, Fe and Al by above-ground parts of maize. The decrease in the uptake of these metals was connected with the decrease in yield, which finds confirmation in other studies [40].

Plant capacity to uptake metals can be used in phytoremediation of industrial waste without harming the environment [21, 41]. The biomass obtained from plants cultivated on substrata fertilized with furnace ash, contaminated with heavy metals, can be assigned for energy purposes [42, 43].

Conclusions

1. Application of ash to the soil, in the amount of 23.33 $g \cdot pot^{-1}$, which corresponded to 20 $t \cdot ha^{-1}$, significantly increased the maize yield. Introduction of ash and increasing doses of cadmium in the amount of 3÷5 $mg \cdot kg^{-1}$ soil DM had significantly increased the yield of the tested plant.

2. Application of subsequent doses of cadmium (7.5÷15 mg·kg^{-1}) caused a reduction in maize yield. Increasing cadmium doses, introduced into soil mixed with ash, increased the content of Cr, Fe, Ni, Cu and Al in above-ground parts and roots of maize, but reduced the content of Mn in the tested plant.
3. Among the studied metals, Mn was translocated from roots to above-ground parts the most efficiently, and Al - the least efficiently, evidence of which are higher values of the translocation factor for Mn than for Al.
4. Introduction of ash to cadmium contaminated soil changed the reaction, which in consequence had an effect on bioavailability of metals for the plants. It was established that above-ground parts of maize took up more Mn and Cu than roots.
5. Elements such as Cr, Fe, Ni and Al were taken up in larger quantities by roots than by above-ground parts of maize.

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Wpływ dodatku popiołu paleniskowego z węgla kamiennego do gleby na fitoprzyswajalność wybranych metali

Badania nad wpływem popiołu paleniskowego z węgla kamiennego na pobieranie Cr, Cu, Ni, Fe, Mn, Al przez kukurydzę (*Zea mays* L.) przeprowadzono w warunkach trzyletniego doświadczenia wazonowego. W doświadczeniu wazonowym zastosowano do gleby uprawnej popiół paleniskowy, w ilości 23,33 g·wazon^{-1}, odpowiadającej 20 t·ha^{-1}, oraz wzrastające dawki kadmu, w ilości 3÷15 mg·kg^{-1} s.m. gleby. Zastosowanie popiołu oraz kadmu w ilości 3÷5 mg·kg^{-1} s.m. do gleby wpłynęło istotnie na zwiększenie plonu części nadziemnych i korzeni kukurydzy. Natomiast zaaplikowanie kolejnych dawek kadmu (7,5÷15 mg·kg^{-1}) spowodowało istotne obniżenie plonu testowanej rośliny. Z badań wynika, że zaaplikowany popiół paleniskowy zmniejszył depresję plonowania kukurydzy. Wprowadzenie popiołu paleniskowego do gleby zanieczyszczonej kadmem wpłynęło na zwiększenie zawartości Cr, Fe, Ni, Cu i Al w biomasie kukurydzy, natomiast wpłynęło na zmniejszenie zawartości Mn

w kukurydzy. Spośród badanych metali najłatwiej był przemieszczany z korzeni do części nadziemnych Mn, a najsłabiej Al, o czym świadczą największe wartości współczynnika translokacji dla Mn, a najmniejsze wartości dla Al. Z badań wynika, że popiół wprowadzony do gleby zanieczyszczonej kadmem nie wpłynął na immobilizację wyżej wymienionych metali, a tym samym nie ograniczył fitoprzyswajalności. Generalnie zanieczyszczenie gleby kadmem i wprowadzenie popiołu stymulowało pobieranie metali przez kukurydzę. Stwierdzono większe pobranie Cr, Fe, Ni i Al przez korzenie, natomiast Mn i Cu przez części nadziemne kukurydzy. Najmniejsze pobranie badanych metali przez kukurydzę zarejestrowano w obiekcie, w którym zastosowano wyłącznie popiół paleniskowy.

Słowa kluczowe: **popiół, Cr, Mn, Fe, Ni, Cu, Al, kukurydza, indeks tolerancji plonu, wskaźnik translokacji metali, zawartość i pobranie metali**