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Effect of bottom ash and soil contamination with cadmium on the chemical composition of maize

Wpływ popiołu paleniskowego i zanieczyszczenia gleby kadmem
na skład chemiczny kukurydzy

Summary. The experiment concerning the effect of furnace waste on the chemical composition of maize was conducted under conditions of a three-year pot experiment. The arable soil was amended with bottom ash in the amount of 23.33 g · pot⁻¹ as well as with increasing doses of cadmium (between 3 and 15 mg · kg⁻¹ soil d.m.). Introduction of ash and cadmium in the amount from 3 to 5 mg · kg⁻¹ d.m. to the soil had a significant effect on the increase of the yield of above-ground parts and roots of maize. The application of cadmium in doses from 7 to 15 mg · kg⁻¹ caused a considerable reduction in the yield of the tested plant. It was shown that the applied furnace ash influenced the decrease in the yielding of maize.

Introduction of furnace ash to cadmium contaminated soil significantly influenced the increase in the content of Na, K, Mg, Ca and Si in maize biomass and the decrease in the content of P in maize. Among the studied elements, K was translocated from the roots to the above-ground parts most efficiently, and Na and Si – least efficiently, the evidence of which are the values of the translocation factor for these elements.

The research shows that ash in cadmium contaminated soil influenced immobilization of phosphorus, and thereby limited the phytoavailability of this element. It was established that the above-ground parts took up more K, Mg, Ca, P, Si with the yield while and maize roots took up more Na. The lowest uptake of the studied metals by maize was observed in the treatment where only furnace ash was applied.

Key words: ash, Na, K, Mg, Ca, P, Si, maize, tolerance index, element translocation factor, uptake of elements

INTRODUCTION

Bioavailability of macroelements depends on soil physical, chemical and biological properties. After application to soil, furnace ash can influence the improvement of soil physicochemical properties, which involves increasing the availability of nutrients for plants [Seshadri *et al.* 2010, Lu *et al.* 2014]. On the other hand, furnace ash used for biological reclamation of landfills constitutes a source of macronutrients for plants [Antonkiewicz and Radkowski 2006, Czech *et al.* 2013, Weber *et al.* 2015]. Apart from macronutrients, ash is a source of microelements and heavy metals, generally bound in minerals which are difficult to dissolve and unavailable for plants [Mazur and Koniecznyński 2004, Smołka-Danielowska 2006]. This waste is also used for binding chemical contaminants in soil [Sitarz-Palczak and Kalembkiewicz 2012, Li *et al.* 2014,]. Maize is an important cultivated species that is used for remediation of chemically contaminated soils [Guo *et al.* 2011, Stanisławska-Głubiak *et al.* 2015]. It can also be a model plant in research in the field of environmental management of industrial waste.

Elements uptake by plants are often directly or indirectly involved in numerous physiological reactions of plants [Bączek-Kwinta *et al.* 2006, Antonkiewicz *et al.* 2016]. Macroelements which have the nature of nutrients favor a proper increase and development of plants, shaping not only the yield but also its quality [Epstein and Bloom 2004]. Application of furnace ash to soil may influence the change in plant chemical composition, by means of a higher uptake of macroelements by plants. Addition of cadmium to soil can be neutralized with furnace ash. Therefore, one can assume that such an environment may have an impact on the uptake of individual macronutrients by plants and their accumulation in tissues. The aim of the research was to determine the effect of furnace ash and increasing doses of cadmium applied to soil on the yield and uptake of Na, K, Mg, Ca, P and Si by maize.

MATERIAL AND RESEARCH METHODS

The research on the effect of furnace ash on the yielding and uptake of Na, K, Mg, Ca, P and Si by maize (*Zea mays* L.), 'Koka' cultivar, was conducted under conditions of a three-year pot experiment.

Soil, furnace ash

Arable soil collected from the humus horizon was used in the experiment. Sand soil contained 95% sand, 2% dust, 3% floatable particles [Systematyka... 2011]. The soil 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°) content of Cr, Cu, Ni, an elevated (I°) content of Pb, was weakly (II°) contaminated with Zn, and moderately (III°) contaminated with Cd (Tab. 1), [Kabata-Pendias *et al.* 1995].

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 [Rozporządzenie... 2014]. 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 lower than provided in the Ordinance of the Ministry of Environment on soil and earth quality standards [Rozporządzenie... 2002]. Special attention was paid in the research to such elements as: Na, K, Mg, Ca, P and Si. These elements are essential for proper growth and development of plants. The content of these elements in the furnace ash was, respectively, over 6, 4, 98, 53, 0.7, 1.9-fold higher than in the soil (Tab. 1).

Table 1. Characteristic physicochemical of soil and ash use in the experiment
Tabela 1. Właściwości fizyczne i chemiczne gleby i popiołu użytych w doświadczeniu

Parameter Parametr	Unit Jednostka	Soil Gleba	Ash Popiół	Scale IUNG* Skala IUNG	Permissible** Wartość dopuszczalna
pH _(KCl)	-	7.06	9.85	-	-
pH _(H2O)	-	7.33	10.06	-	-
Texture Uziarnienie	-	sand soil/ piasek luźny	sandy silty loam silt/ glina piaszczysta pyłasta	-	-
Cr		5.48	33.85	0	150
Zn		251.25	93.75	II	300
Pb		45.10	18.65	I	100
Cu	mg · kg ⁻¹	6.00	74.50	0	150
Cd	d.m./s.m.	2.75	0.28	III	4
Ni		3.38	39.98	0	100
Si		296.5	884.8	-	-
Na		0.11	0.82	-	-
K	g · kg ⁻¹	0.19	1.09	-	-
Mg	d.m./s.m.	0.11	10.95	-	-
Ca		0.39	21.28	-	-
P		0.03	1.96	-	-

* 0 natural content/ zawartość naturalna, I elevated content/ zawartość podwyższona, II slight content/ słabo zanieczyszczona, III medium content/ średnio zanieczyszczona;

** Permissible content according to Rozporządzenie...[2002]/ Wartość dopuszczalna według Rozporządzenia... [2002]

Scheme and conditions 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 (from 3.0 to 15.0 mg · kg⁻¹ d.m.), and treatment 9 consisted of furnace ash only. Furnace ash in the amount of 23.33 g · pot⁻¹, which theoretically corresponded to 20 Mg d.m. · 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 furnace ash and cadmium in the form of aqueous solution of 3CdSO₄ · 8H₂O. Cadmium is a metal that is chemically quite active, and cadmium sulfate solution is bioavailable and toxic for plants [Kim *et al.* 2015, Sharma and Sachdeva 2015].

Table 2. Yield and tolerance index (TI) of maize
Tabela 2. Plon oraz indeks tolerancji (TI) plonu kukurydzy

Number treatment* Numer obiektu	Doses Cd /ash Dawka Cd/popioł	Yield (g d.m. · pot ⁻¹) Plon (g s.m. · wazon ⁻¹)			Tolerance index (TI)** Indeks tolerancji		
		1st***	2nd	3rd	1st	2nd	3rd
		above ground parts części nadziemne			above ground parts części nadziemne		
1	control kontrola	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 $\alpha \leq 0.01$ / NRI $\alpha \leq 0,01$		2.53	2.76	7.54	-	-	-
		Roots/ Korzenie			Roots/ Korzenie		
1	control kontrola	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 $\alpha \leq 0.01$ / NRI $\alpha \leq 0,01$		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/ Obiekty: 1 – kontrola, 2 – gleba + popioł, 3 – 3 mg Cd + popioł, 4 – 4 mg Cd + popioł, 5 – 5 mg Cd + popioł, 6 – 7,5 mg Cd + popioł, 7 – 10 mg Cd + popioł, 8 – 15 mg Cd + popioł, 9 – wyłącznie popioł

** TI – 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)/ Indeks tolerancji plonu wyliczony jako iloraz plonu uzyskanego na glebie zanieczyszczonej (obiekty 2–9) i plonu uzyskanego w obiekcie kontrolnym (obiekt 1)

*** Years/ Lata

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 · kg⁻¹ soil d.m., in the form of NH₄NO₃, KH₂PO₄, 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, and after drying at 105°C, the amount of yield of the absolutely dry matter was determined and expressed in g d.m. · pot⁻¹.

Determinations, calculations and statistical analysis of the results

After mineralization at 550°C (from each repetition), Na, K, Mg, Ca, P and Si were determined in plant material using the ICP-OES method. It presents the content of these elements in above-ground parts and roots of maize as a weighted mean from three years of research (Fig. 1, 2). The annual uptake of elements (U_e) was calculated as the product of dry matter yield (Y) and the element content (C), according to the formula: $U_e = Y \cdot C$. The uptake of elements by above-ground parts and roots of maize is presented as the sum from three years of research (Fig. 2). Tolerance index (TI) was calculated as a ratio of the yield obtained on contaminated soil to the yield obtained in the control treatment (Tab. 2). The element translocation factor (TF) was calculated as a ratio of the content of the element in above-ground parts to its content in roots (Tab. 3). The paper also shows relationships between the studied macroelements in above-ground parts of maize. K : Na, K : Ca, K : Mg, K : (Ca + Mg), Ca : Mg proportions were calculated equivalently, whereas Ca:P by weight. After completion of the experiment, soil pH was determined potentiometrically in 1 mol · dm⁻³ KCl.

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 the elements 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 $p < 0.01$.

RESEARCH RESULTS

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). Depending on treatment and year of the research, the yield of above-ground parts varied from 13.08 to 43.02 g d.m., and in the case of roots – from 2.79 to 10.60 g · pot⁻¹ (Tab. 2).

The highest yield of maize above-ground parts (43.02 g d.m.) was obtained on soil with ash amendment (treatment 2), and the lowest (13.08 g d.m.) in the treatment where only ash was applied (treatment 9). Difference in yielding between these treatments reached over 29.94 g d.m. · pot⁻¹ for above-ground parts, and 7.81 g d.m. · pot⁻¹ in the case of roots. The research shows that the addition of ash to light soil (treatment 2) had a significant effect on the increase in the amount of yield of above-ground parts and 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 · kg⁻¹ soil d.m. (treatments 3–5) did not have a significant effect on maize yield. The determined stability of maize yielding in the above-mentioned treatments may be explained by, among other things, a positive effect of ash alone on physicochemical properties of the light soil, 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).

The increase in soil contamination with cadmium from 7.5 to 10 mg · kg⁻¹ soil d.m. (treatments 6–7) caused a reduction in maize yield, although it was not statistically significant.

Cadmium applied to the soil in the amount of 15 mg · kg⁻¹ soil d.m. (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 for roots – 20%, 15%, 19% in relation to the control. Application of ash alone (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 ash and cadmium to the soil, which can be explained by improvement of physical and chemical properties of the soil, a reduction in cadmium solubility, and thereby a reduction in phytoavailability of this metal.

Tolerance index (TI)

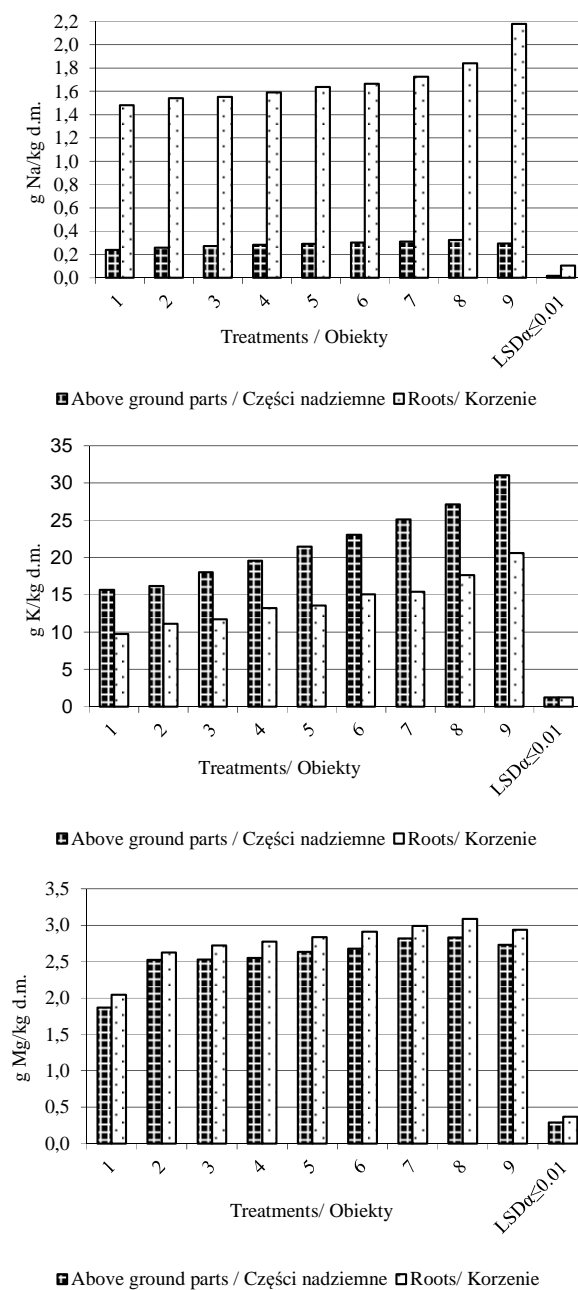
Maize sensitivity to the presence of furnace ash and cadmium in the soil was determined based on tolerance index. In recent years, tolerance index (TI) has been regarded as the most reliable indicator for determining compounds which are toxic for plants in soils [Wilkins 1978, Audet and Charest 2007]. Tolerance index may assume values $TI < 1$, $TI = 1$, $TI > 1$. If this index is less than one, it implies growth inhibition of plants, and sometimes their total death. When 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.

Calculations show that TI for maize yield had values over 1 in treatments 2–5, where ash and cadmium were amended to soil in doses of 3–5 mg · kg⁻¹ soil d.m. (Tab. 2). Value of the index below 1 was determined in the treatments where cadmium was added in doses from 7.5 to 15 mg · kg⁻¹ d.m. (treatments 6–8), and the lowest TI value was obtained in the treatment amended only with furnace ash (treatment 9). The presented research shows that TI was determined by cadmium dose (treatments 6–8) and by 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) showed a beneficial effect on plant yielding. It has been also shown that the addition of ash to the cadmium contaminated soil alleviated the effects of heavy metals present in the soil.

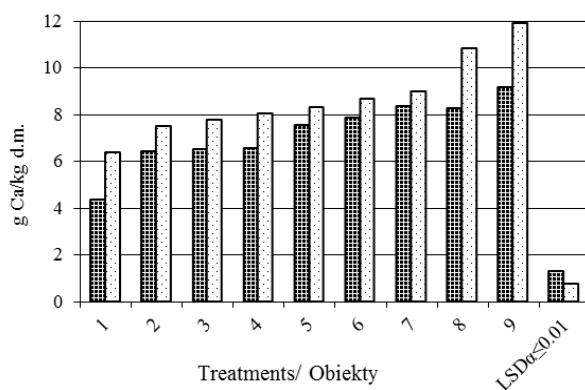
The content of Na, K, Mg, Ca, P and Si in maize

The following were assumed as indicators of cadmium and ash interaction with the studied elements: content, translocation, uptake, and relationships between macroelements in maize.

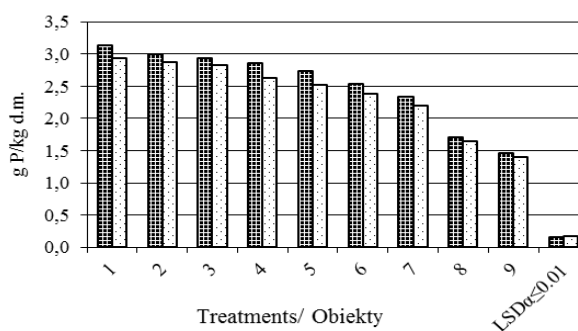


See Table 2 for explanation of symbols treatments/ objaśnienia – patrz tabela 2

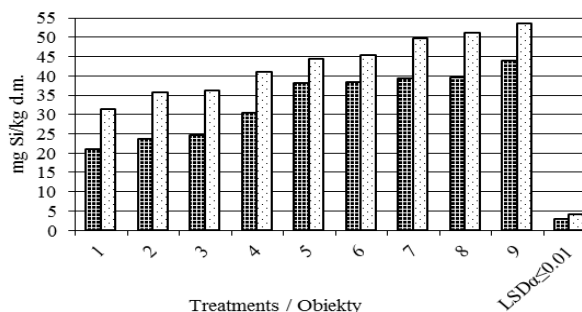
Fig. 1. Content of Na, K, Mg in maize
Rys. 1. Zawartość Na, K, Mg w kukurydzy



■ Above ground parts / Części nadziemne ▨ Roots/ Korzenie



■ Above ground parts / Części nadziemne ▨ Roots/ Korzenie



■ Above ground parts / Części nadziemne ▨ Roots/ Korzenie

See Table 2 for explanation of symbols treatments/ objaśnienia – patrz tabela 2

Fig. 2. Content of Ca, P, Si in maize
Rys. 2. Zawartość Ca, P, Si w kukurydzy

The content of the studied elements was determined by the analyzed part of the plant, treatment, including the degree of its contamination with cadmium (Fig. 1, 2). Taking into account the distribution of individual elements in maize, no unambiguous tendency was observed. Na and K showed the greatest disproportions between the content in roots and above-ground parts; Si showed smaller disproportions; and the smallest disproportions were observed for Mg, Ca and P. Analysis of the chemical composition of maize indicates that maize above-ground parts had a higher content of K and P, whereas roots had a higher content of Na, Mg, Ca and Ti.

When comparing the chemical composition of maize from the control (treatment 1) and from the treatment with ash amendment (treatment 2), it needs to be said that the studied waste was a significant source of nutrients. The addition of ash to the soil (treatment 2) increased the content of Na, K, Mg, Ca and Si in maize above-ground parts, and reached, respectively, over: 8%, 3%, 35%, 47%, and 11% in relation to the control. The research indicates that application of furnace ash to the soil influenced the increase in the content of Ca and Mg to the greatest extent, then Si, and Na and K — to the smallest extent. An inverse relationship was observed for phosphorus. Furnace ash applied to the soil decreased the content of this element in the tested plant.

Cultivation of maize on ash only was another confirmation that ash can be an important source of nutrients for this plant (Fig. 1, 2, treatment 9). The research shows that maize grown on the control soil (treatment 1) had a considerably lower content of Na, K, Mg, Ca and Si in relation to maize from treatment 9 (only ash). The increase in the content of Na, K, Mg, Ca and Si in above-ground parts of maize grown on ash alone reached, respectively, over 22%, 98%, 46%, 110%, 108% as compared with the control treatment. Maize grown on ash alone contained over 53% less P as compared with the control treatment.

A significant part of the conducted research was to determine what effect the level of soil contamination with cadmium had on the uptake of monovalent cations (Na, K), divalent cations (Ca, Mg), a phosphate anion (P) and silicon (Si) in the form of silicic acid.

Analysis of the chemical composition of maize fertilized with ash with the addition of cadmium (treatments 3–8) points to considerable differences in its chemical composition compared with plants from the control treatment. The increased soil contamination with cadmium (3–15 mg Cd · kg⁻¹ soil d.m.) had a significant impact on the uptake of monovalent cations (Na and K) and divalent cations (Ca and Mg). The increase in Na content for above-ground parts ranged from 13.3 to 35.4% in relation to the control treatment and from 4.9 to 24.4% for roots. In the case of K, a higher effect of the increase in the content of this element under the influence of contamination with cadmium was recorded. The increase in K content in above-ground parts of maize, as the level of soil contamination with cadmium increased, varied from 15.1% to 73.2%, and in roots — from 20.2% to 81.7%. In the case of divalent cations, soil contamination with cadmium (3–15 mg Cd · kg⁻¹ soil d.m.) had a greater effect on the increase in Ca content in maize in comparison with Mg.

Increasing doses of cadmium in the soil (treatments 3–8) also led to an increase in the content of silicon in maize. The increase in Si content for above-ground parts ranged from 16.3 to 88.0% compared with the control treatment, whereas increase for roots was lower and varied between 15.4% and 62.6% as compared with the control treatment.

Presence of ash and cadmium in the substrate decreased the P content in above-ground parts and roots of maize. It was established that as cadmium dose in the soil increased, there was a systematic reduction in P content in maize. At the highest dose of cadmium in the soil (treatment 8), the decrease in P content in above-ground parts and roots exceeded 43% compared with the control treatment.

The experiment revealed positive strong correlations between the dose of cadmium introduced to the soil fertilized with ash and the content of Na, Mg, Ca and Si in above-ground parts of maize ($r = 0.43-0.78$) as well as the content of Mg and Si in roots ($r = 0.52-0.57$). The research also shows that introduction of cadmium to the soil fertilized with furnace ash was negatively correlated with P content in above-ground parts and roots of maize, but that relationship was not confirmed statistically ($r = -0.40$). Reaction of the substrate had a significant effect on the content of macronutrients in maize. Strong positive correlations were determined between soil reaction and the content of K and Ca in maize above-ground parts ($r = 0.60-0.42$) as well as the content of Na, K, Ca and Si in maize roots ($r = 0.81-0.44$). The calculated correlation coefficient also points to a significant negative correlation between soil reaction and P content in above-ground parts and roots of maize ($r = 0.63-0.62$).

Translocation factor of an element in the plant (TF)

Mobility of the studied elements in the plant was determined using the translocation factor (TF). This parameter represents the ratio of the content of an element in above-ground parts to its content in roots [Park *et al.* 2011]. Relationships between the content of Na, K, Mg, Ca, P and Si in above-ground parts and roots are presented in Table 3.

Table 3. Translocation Factor of elements in the plant (TF)
Tabela 3. Wskaźnik translokacji pierwiastków w roślinie (TF)

Number treatment* Numer obiektu	Doses Cd/ash Dawka Cd/popiół	pH _{KCl} soil pH _{KCl} gleby	Translocation Factor (TF) Wskaźnik translokacji					
			Na	K	Mg	Ca	P	Si
1	control/ kontrola	6.94	0.16	1.61	0.91	0.68	1.07	0.68
2	0 + A	6.98	0.17	1.46	0.97	0.86	1.05	0.66
3	3 + A	6.98	0.18	1.55	0.93	0.84	1.04	0.68
4	4 + A	6.93	0.18	1.49	0.93	0.82	1.09	0.74
5	5 + A	6.91	0.18	1.59	0.93	0.91	1.09	0.86
6	7,5 + A	6.86	0.18	1.54	0.92	0.91	1.06	0.85
7	10 + A	6.85	0.18	1.63	0.95	0.93	1.06	0.79
8	15 + A	6.79	0.18	1.54	0.92	0.76	1.04	0.78
9	A	9.70	0.14	1.51	0.93	0.77	1.04	0.82
Mean/ Średnia		7.21	0.17	1.54	0.93	0.83	1.06	0.76
V %		12.95	8.44	3.60	1.74	9.71	1.85	9.96
LSD $\alpha \leq 0.01$ NIR $\alpha \leq 0,01$		0.105	0.012	0.133	0.176	0.144	0.073	0.096

* See Table 2 for explanation of symbols/ objaśnienia patrz tabela 2

** TF Translocation Factor of metal calculated as the quotient of the metal content of the aerial parts to the content in the roots/ Wskaźnik translokacji metalu wyliczony jako iloraz zawartości metalu w częściach nadziemnych i zawartości metalu w korzeniach

The highest variability of the translocation factor (TF) was recorded in the case of Si and Ca, and the lowest in the case of Mg and P. A higher accumulation of the elements in maize roots in relation to above-ground parts is confirmed by low values of translocation factor (TF) of an element (Tab. 3). Among the studied elements, K moved from roots to above-ground parts to the greatest degree, the evidence of which is the highest value of translocation factor (TF). Based on the mean value of translocation factor (TF), mobility of the elements in maize was arranged in the following order: $K < P < Mg < Ca < Si < Na$. The research shows that Na had the lowest mobility in the plant, which means that this element is accumulated mainly in roots.

It has been shown that increasing cadmium doses in the soil were significantly positively correlated with the translocation factor only for Na ($r = 0.54$). Soil reaction also was negatively correlated only with the translocation factor for Na ($r = -0.84$). A negative correlation was observed in the experiment between P content in above-ground parts and roots of maize and translocation factor for Si ($r = 0.47-0.51$). The content of the other macroelements (Na, K, Ca, Si) in maize was positively correlated with translocation factor for Si ($r = 0.48-0.81$). The content of Ca and Mg in above-ground parts of maize was positively correlated with translocation factor for these elements ($r = 0.52-0.58$).

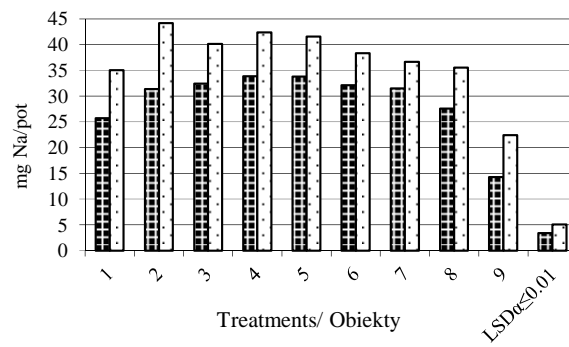
Uptake of Na, K, Mg, Ca, P and Si by maize

The uptake of elements by maize depended on the amount of yield, including the index part of the plant, as well as on the level of soil contamination with cadmium (Fig. 3, 4, Tab. 2). It was established that above-ground parts of maize took up more K, Mg, Ca, P and Si than roots. Higher uptake of these elements by above-ground parts of maize was associated with a more than four times higher yield of this part of plant compared with roots (Tab. 2). In the case of Na, an inverse relationship was determined. Maize roots took up more Na than above-ground parts. The higher uptake of Na 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 of maize (Fig. 3, 4). The research shows that introduction of cadmium to the soil fertilized with furnace ash was positively correlated with the uptake of K, Ca and Si ($r = 0.44-0.60$). Uptake of Na, K, Mg, Ca, P and Si by above-ground parts and roots of maize was significantly negatively correlated with soil reaction ($r = 0.54-0.85$). Strict interdependencies between the content of macroelements in above-ground parts and roots of maize and their uptake by index parts of the tested plant were also observed ($r = 0.49-0.92$).

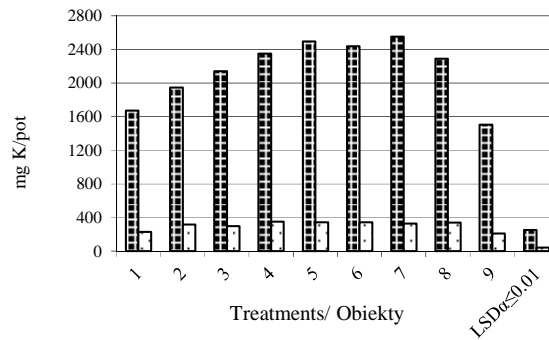
Relationships between macronutrients in maize

In agricultural practice, quality of plants (including fodders) is frequently evaluated based on weight or equivalence ratio between elements. The effect of ash and increasing doses of cadmium on the value of the ratio between macroelements in above-ground parts of maize is presented in the paper for cognitive purposes. Data presented in Table 4 indicate that application of ash and of increasing doses of cadmium to the soil significantly modified the ratios between macroelements.

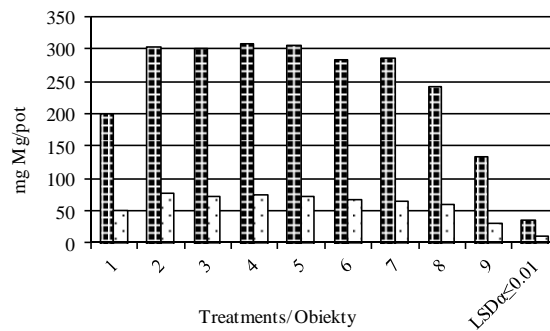
A considerable range of variability in the ratios between elements in above-ground parts of maize was observed. This suggests that maize grown on soil with ash amendment and with increasing doses of cadmium was extremely tolerant to quantitative relations



■ Above ground parts / Części nadziemne □ Roots/ Korzenie



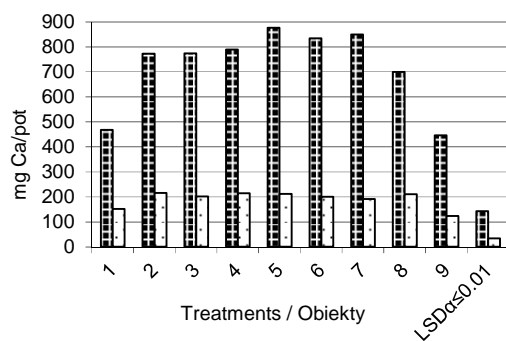
■ Above ground parts / Części nadziemne □ Roots/ Korzenie



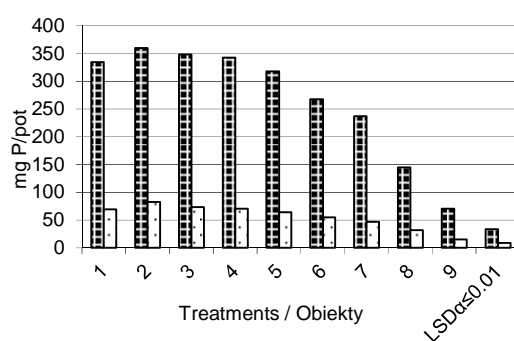
■ Above ground parts / Części nadziemne □ Roots/ Korzenie

See Table 2 for explanation of symbols treatments/ objaśnienia – patrz tabela 2

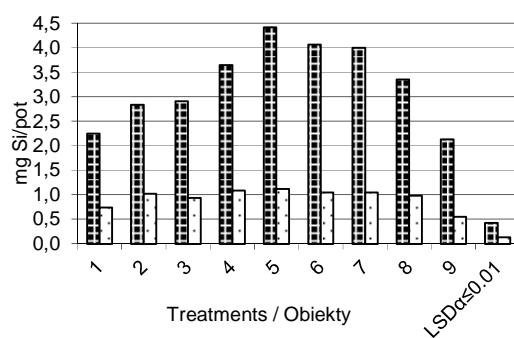
Fig. 3. Uptake of Na, K, Mg by maize
Rys. 3. Pobranie Na, K, Mg przez kukurydzę



■ Above ground parts / Części nadziemne □ Roots / Korzenie



■ Above ground parts / Części nadziemne □ Roots / Korzenie



■ Above ground parts / Części nadziemne □ Roots / Korzenie

See Table 2 for explanation of symbols treatments/ Objaśnienia patrz tabela 2 numery obiektów

Fig. 4. Uptake of Ca, P, Si by maize
Rys. 4. Pobranie Ca, P, Si przez kukurydzę

Table 4. Relationships between macronutrients in maize
Tabela 4. Proporcje pomiędzy pierwiastkami w kukurydzy

Number Treatment* Numer Obiektu	Doses Cd/ash Dawka Cd/popiół	Ratio/ Stosunek					
		Ca : P	Ca : Mg	K : Mg	K : Ca	K : Na	K : (Ca + Mg)
1	control kontrola	1.39	1.41	2.60	1.85	38.28	1.08
2	0 + A	2.15	1.54	1.99	1.30	36.57	0.79
3	3 + A	2.23	1.56	2.21	1.42	38.95	0.86
4	4 + A	2.30	1.56	2.39	1.53	40.87	0.93
5	5 + A	2.76	1.74	2.54	1.48	43.49	0.93
6	7,5 + A	3.11	1.79	2.69	1.52	44.70	0.97
7	10 + A	3.59	1.80	2.79	1.55	47.80	1.00
8	15 + A	4.84	1.77	2.98	1.69	49.01	1.08
9	A	6.31	2.04	3.52	1.73	62.02	1.16
V %		48.20	11.11	16.97	10.82	17.43	11.94
LSD $\alpha \leq 0.01$ NRI $\alpha \leq 0,01$		0.631	0.208	0.297	0.278	3.929	0.144

* See Table 2 for explanation of symbols/ objaśnienia – patrz tabela 2

between these elements. The greatest variability was observed in the case of Ca : P ratio, whereas the lowest variability in the case of K : Ca ratio. The calculated ratios between Ca : P, Ca : Mg, K : Mg, K : Na, K : (Ca + Mg) were narrowest in the control treatment, and under the influence of ash and increasing doses of cadmium in the soil they underwent considerable widening.

Quality of plant material depends not only on the optimum content of mineral components, but also on mutual ratios between them. During theoretical estimation of fodder in terms of its nutritional value, K : Na ratio should be 10:1, whereas the optimum value of Ca : P and Ca:Mg ratios is determined at a level of 2:1 and 3:1, respectively. Good quality fodder should have optimal ratios amounting to K: (Ca + Mg) = 1.6–2.2; K : Mg = 6 : 1; K : Ca = 2 : 1 [Czuba and Mazur 1988, Falkowski *et al.* 2000, Wyszowski 2002]. The calculated equivalence ratios for K : Mg, Ca : Mg, K : (Ca + Mg), obtained in the control treatment, did not exceed optimal value given by the above-quoted authors, whereas K : Ca ratio was close to optimal. K : Na ratio was unfavorable, exceeding the permissible value of 10. Numerous authors [Czuba and Mazur 1988, Mackowiak *et al.* 2011] state that higher uptake of K by plants is often connected with a simultaneous decrease in sodium absorption. Underwood [1971], however, points to the lack of convincing data on the harmfulness of the ratio of these elements amounting to as much as 50 : 1 (but provided that Na is present in fodder in the amount that will ensure the proper course of physiological processes) to animals.

No strong correlation was observed in the experiment between the dose of cadmium in the soil fertilized with ash and the studied ratios (Ca : P, Ca : Mg, K : Mg, K : Ca, K : Na, K: (Ca + Mg)) in maize. Reaction of the soil fertilized with ash and cadmium was

positively strongly correlated with Ca : P, Ca : Mg, K : Mg, K : Na, K: (Ca + Mg) ratios in maize ($r = 0.47\text{--}0.77$). It was observed in the experiment that the content of macronutrients in above-ground parts and roots of maize was strongly correlated with the following ratios: Ca : P, Ca : Mg, K : Mg, K : Na, K: (Ca + Mg); the value of correlation coefficient ranged from $r = 0.46$ to 0.96 . No strong correlation between the content of macronutrients in maize and K : Ca ratio was observed. A negative strong correlation between the uptake of Na, K, Ca, Mg and P by maize and the calculated ratios between these elements ($r = 0.44\text{--}0.91$) was recorded during the experiment.

DISCUSSION

Our research shows that furnace ash increases the yield of cultivated plants, mainly as a result of improvement of physical and chemical properties of the substrate, which is confirmed in other authors' research [Gupta *et al.* 2002, Mondol *et al.* 2012]. Addition of ash to soil also has an immobilizing effect on cadmium and other heavy metals soluble in the soil solution [Sakamoto *et al.* 2001, Li *et al.* 2014]. Immobilization of heavy metals in soil reduces their unfavorable effect on plants [Kołodziej *et al.* 2016].

Furnace ash constitutes a potential source of macronutrients for plants. Therefore special attention was paid in the research to such elements as: Na, K, Mg, Ca, P and Si. Selection of these elements was well-founded due to the fact that ash and cadmium in increasing doses influence the uptake of macroelements by plants [Kusznierewicz *et al.* 2012, Rolka 2015].

Ash derived from combustion of bituminous coal, in optimal dose, becomes a source of nutrients which are transferred to the soil solution and to the soil sorption complex. This may lead to an increase in nutrient bioavailability [Gupta *et al.* 2002, Paleckienė *et al.* 2010]. A substantial number of elements of the ash matrix occur in silicate minerals, which reduces their solubility in water, and thereby renders them less available for plants [Ratajczak *et al.* 1999, Rivera *et al.* 2015].

In our research, favorable changes in the content of Na, K, Ca, Mg and Si in maize were observed, which was indicative of good fertilizer value of the studied ash. The addition of ash to the cadmium contaminated soil caused alkalization of the substrate (Tab. 3), and in consequence an increase in bioavailability of macroelements (except phosphorus), which was confirmed by other authors [Sakamoto *et al.* 2001, Prado *et al.* 2002]. However, the effect of cadmium on the increase in content of the studied elements in maize requires further investigations in order to explain the mechanism of this process. Moreover, one should consider the possibility of using ash in revitalization of chemically degraded soils, bearing in mind ash as a source of nutrients, a deacidifying agent, and an agent reducing availability of heavy metals.

Studies [Demeyer *et al.* 2001] confirm the obtained results regarding alkalization of the soil environment and the considerable effect of ash on phosphorus fixation in soil (the evidence of which is the amount of phosphorus taken up by plants). In our research, increasing cadmium doses in treatments with ash amendment also reduced the uptake of phosphorus by maize, which may have a connection with chemical sorption of phosphorus [Gray and Schwab 1993, Gupta *et al.* 2002]. Research on the chemical composition of ash, conducted by Ratajczak and others [1999] suggests that in the analyzed ash de-

rived from bituminous coal phosphorus occurs in compounds that are not readily available for plants. Phosphorus may also be a component of silicate structures, and P^{3+} ions can substitute Si^{4+} in silicate structures of ash.

Silicon is generally poorly mobile in soil, but in certain conditions it can be bioavailable [Szulc *et al.* 2015]. In addition, this element is a common component of plants, and its variable content is associated both with the effect of soil factors and with properties of plants [Gascho 2001]. Some plants accumulate greater amounts of silicon, improving plant resistance to the chemical stress of the substrate [Tripathi *et al.* 2013]. In general, solubility of silicon increases along with soil pH value, and is the highest within alkaline range [Sanglard *et al.* 2014]. The results of our research confirm this dependence, i.e. the increase in silicon availability for plants after application of ash to the soil. The content of silicon in ash also modifies other constituents of ash. Strong correlations between Si content in maize and Ca and Mg content in the tested plant were observed. Research conducted by Rivera *et al.* [2015] confirms that Ca in ash was strongly correlated with Si, which is the major constituent of this waste. On the other hand, other studies point to a synergistic effect of Si and P in detoxification of chemical contaminants in soil [Sanglard *et al.* 2014, Szulc *et al.* 2015].

Research carried out by Antonkiewicz [2010] suggests that furnace increased the content of macroelements in plant biomass and broadened the ratios between elements. Changes in ratios between macroelements in the plant biomass may result from a higher demand, and thereby a higher uptake of macroelements under stress conditions, with chemical contamination of the substrate [Bączek-Kwinta *et al.* 2008]. The change in ratio between the elements in maize biomass was a result of alkalization of the substrate, which in consequence conditioned the concentration of individual elements in the soil solution, and thereby changed the availability of the elements by maize [Demeyer *et al.* 2001]. In our research, it was found that the addition of ash and cadmium to the soil had a significant effect on the widening of ratios between elements. Widening of these ratios is believed to be more beneficial in terms of fodder quality [Płodzik 1996].

Ash, on account of its physical and chemical properties, can be used as a source of monovalent cations (Na and K) and divalent cations (Ca and Mg), as well as for immobilization of phosphorus in the substrate.

CONCLUSIONS

1. The addition of ash to the soil in a dose of $20 \text{ t} \cdot \text{ha}^{-1}$ as well as the addition of cadmium in a dose from 3.0 to $5.0 \text{ mg} \cdot \text{kg}^{-1}$ soil d.m. significantly increased the yield of maize dry matter.
2. Cadmium in increasing doses increased the content of Na, K, Mg, Ca and Si in above-ground parts and roots of maize, but decreased P content in the tested plant.
3. From the studied elements, K was most easily transferred from roots to above-ground parts, and Na – the least easily.
4. It was established that above-ground parts of maize took up more K, Mg, Ca, P and Si than roots, with the exception of Na.

5. The research shows that ash, on account of its physical and chemical properties, can be used as a source of nutrients for plants, particularly the ones grown on industrial waste, chemically contaminated substrates.

6. It was shown that the addition of ash and cadmium to the soil had a significant effect on widening of the ratios between macroelements in maize.

7. The obtained results point to the need for continuing research aiming at explaining the mechanisms connected with the uptake of Na, K, Mg, Ca, Si and P by plants, under conditions of chemical stress.

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Streszczenie. Badania nad wpływem odpadu paleniskowego na skład chemiczny kukurydzy (*Zea mays* L.) przeprowadzono w warunkach trzyletniego doświadczenia wazonowego. Do gleby uprawnej zastosowano popiół paleniskowy, w ilości 23,33 g · wazon⁻¹, oraz wzrastające dawki kadmu, w ilości od 3 do 15 mg · kg⁻¹ s.m. gleby. Wprowadzenie popiołu oraz kadmu w ilości od 3 do 5 mg · kg⁻¹ s.m. do gleby wpłynęło istotnie na zwiększenie plonu części nadziemnych i korzeni

kukurydzy. Natomiast zaaplikowanie kadmu w dawkach od 7 do 15 mg · kg⁻¹ spowodowało istotne obniżenie plonu testowanej rośliny. Wykazano, że zaaplikowany popiół paleniskowy wpłynął na depresję plonowania kukurydzy. Wprowadzenie popiołu paleniskowego do gleby zanieczyszczonej kadmem wpłynęło istotnie na zwiększenie zawartości Na, K, Mg, Ca i Si w biomacie kukurydzy oraz na zmniejszenie zawartości P. Spośród badanych pierwiastków najłatwiej był przemieszczany z korzeni do części nadziemnych K, a najsłabiej Na i Si, o czym świadczą wartości współczynnika translokacji dla tych pierwiastków. Z badań wynika, że popioły w glebie zanieczyszczonej kadmem wpłynęły na immobilizację fosforu, a tym samym ograniczyły fitoprzyswajalność tego pierwiastka. Stwierdzono większe pobranie K, Mg, Ca, P, Si z plonem przez części nadziemne, a Na przez korzenie kukurydzy. Najmniejsze pobranie badanych metali przez kukurydzę zarejestrowano w obiekcie, w którym zastosowano wyłącznie popiół paleniskowy.

Słowa kluczowe: popioły, Na, K, Mg, Ca, P, Si, kukurydza, indeks tolerancji plonu, wskaźnik translokacji pierwiastka, pobranie pierwiastków