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SOIL POLLUTION WITH ARSENIC VERSUS THE CONCENTRATION OF MAGNESIUM IN PLANTS

WP£YW ZANIECZYSZCZENIA GLEBY ARSENEM NA ZAWARTOŚĆ MAGNEZU W ROŚLINACH

Abstract: A study has been carried out in order to determine the effect of soil pollution with arsenic on the concentration of magnesium in plants. Soils under yellow lupine were contaminated with arsenic at the rates of 10, 20, 30 and 40 mg As \cdot kg⁻¹ and those sown with maize, cocksfoot, spring barley and swedes received 25, 50, 75 and 100 mg As \cdot kg⁻¹. The following substances were used to neutralize the effect of arsenic on plants: compost, lime, charcoal, loam and natural zeolite in the trials with maize and, additionally, synthetic zeolite in the experiments on cocksfoot and yellow lupine or peat, loam, pinewood bark, dolomite and synthetic zeolite in the trials with spring barley and swedes. The influence of increasing soil pollution with arsenic on the concentration of magnesium in particular organs of the test plants was varied. In general, the content of magnesium in plant parts tended to be positively correlated with the degree of soil contamination with arsenic. It also depended on the plant's species and organ as well as the type of a neutralizing agent applied. Positive correlation was discovered for the roots and aboveground parts of maize, cocksfoot and yellow lupine as well as grain, straw and roots of spring barley. Changes in the magnesium levels caused by arsenic pollution were larger in the roots than in the aboveground parts of plants, especially in the case of spring barley. A decrease in the magnesium concentration in plant tissues caused by soil contamination with arsenic was noticed only in the roots and aboveground parts of swedes. The neutralizing substances produced the strongest positive effect on the content of magnesium in the aboveground parts of maize and roots of cocksfoot. With regard to the remaining plant species, this effect was much weaker.

Keywords: arsenic contamination, neutralizing substances, plants, magnesium content

Human activity is the main source of environmental pollution with arsenic. Han et al [1] distinguish two anthropogenic paths of introducing arsenic to matter cycling in nature. One relies on extracting arsenic from geological deposits rich in this element. The other one is when arsenic is introduced to environment as a by-product of extracting metal ores or bioliths which contain arsenic compounds. By using and

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recycling products comprising arsenic as well as non-iron metals and combustion of bioliths we release arsenic to environment. Point accumulation of excessive arsenic levels in nature is caused by a variety of human actions, including industrial activities, and particularly metallurgy, energy generation, glass production and chemical industry. Other essential sources of arsenic in nature include agriculture and improper municipal or industrial waste dumping [2, 3]. According to the WHO [3], the main cause of water, air and soil pollution with arsenic is extraction and processing of non-iron metals, especially copper, lead, silver and gold. Adverse effects produced by arsenic on plants depend in several factors, of which the major ones are the level of contamination, plant species and type of soil [4, 5]. One of the most typical symptoms of the toxic effect of arsenic is severe dwarfing of plants [2]. Arsenic contamination of soil can modify very extensively plant germination, growth and development; it can also raise concentration of arsenic in plant tissues and cause disorders in the uptake of macro- and micronutrients. In conclusion to the above, it can be stated that the uptake of arsenic by plants should be limited.

The objective of the present study has been to determine the effect of soil pollution with arsenic on the content of magnesium in plants. Soil contamination with arsenic and its consequences were examined in conjunction with the addition of several neutralizing agents to soil.

Material and methods

The study was based on 5 pot experiments, which were performed in a greenhouse at the University of Warmia and Mazury in Olsztyn (Poland). The soils taken for the trials were similar in physicochemical properties (Table 1). All the soils were derived from the Ap humus layer of typical brown soil characterized by the granulometric composition of light loamy sand. The reaction of the soils was acidic or slightly acidic. The pots were filled with 9 kg soil each. The effect produced by arsenic (as an aqueous solution of sodium arsenate) was tested on: maize (*Zea mays* L.) cv. Scandia, cocksfoot (*Dactylis glomerata* L.) cv. Nawra, yellow lupine (*Lupinus luteus* L.) cv. Juno, spring barley (*Hordeum vulgare* L.) cv. Ortega and fodder swedes (*Brassica napus* var. *napobrassica*) cv. Sara. In all the trials (except yellow lupine) soil contamination with arsenic was at the level of 0, 25, 50, 75 and 100 mg As \cdot kg⁻¹ soil. For the experiments on yellow lupine the soil contamination rates were: 0, 10, 20, 30 and 40 mg As \cdot kg⁻¹ soil. The neutralizing agents introduced to soil in the experiments involving cocksfoot and yellow lupine were: lime, natural zeolite, charcoal, loam, compost and synthetic zeolite. The same substances but synthetic zeolite were used in the studies on maize. In the trials on barley and swedes the following neutralizing substances were applied: peat, pinewood bark, loam, dolomite and synthetic zeolite. All the neutralizing agents were added to soil at a ratio of 3 % to the soil mass in a pot, except lime and dolomite, which were used in quantities corresponding to 1 hydrolytic acidity (Hh). In order to provide for the nutritional demands of the crops, the soils also received NPK fertilization. Nitrogen was added to the soils as urea, phosphorus in the form of triple superphosphate and potassium as potassium salt. Prior to the application, all the fertilizers had been

					Some chemical properties of soils used for pot trials														
	$_{\rm pd}$										Total forms						Available forms		
Trials	Ξ	$\Xi.$	$[\text{mmol}\cdot\text{kg}^{-1}]$ Ê	\cup	z	\sim	×	$\mathop{\rm Mg}\nolimits$	ී	\mathbb{Z}	As	්	\mathbb{Z}	Мn	ĒΘ	\sim	ĸ	Mg	
	$\rm H_2O$	KCI		$[{\bf g} \cdot {\bf k} {\bf g}^{-1}$ (dm]			$[g \cdot kg^{-1} d.m.]$				$[\text{mg} \cdot \text{kg}^{-1}]$			$[s\cdot kg^{-1}]$		$[\text{mg} \cdot \text{kg}^{-1}]$		
With maize	6.07	5.91	19.5	5.01	0.61	0.43	0.52	0.41	1.10	0.09	2.71	1.58	24.34	272.22	10.70	53.2	94.5	34.0	
and yellow lupine With cocksfoot	5.75	4.53	33.1	5.41	0.69	0.47	0.96	0.51	1.41	0.11	3.58	1.44	22.81	253.83	12.50	49.8	87.2	34.2	
With barley and swedes	5.53	4.16	28.2	5.48	0.51	0.45	0.88	0.55	1.35	0.08	2.21	1.51	23.15	258.77	12.59	52.2	91.8	29.9	
																		\mathcal{L} Table	
				Chemical composition of materials (supplements) used for arsenic inactivation															
										Elements									
Materials			\sim	⊻		Mg	Ca		\mathbf{z}		As		Εe		Мn	්		\mathbb{Z}	
					$[g \cdot kg^{-1}$ d.m.										$\left[\text{mg} \cdot \text{kg}^{-1} \, \text{d.m.}\right]$				
Compost			2.72	1.58		1.56	18.21		0.14		2.55		368		72.55	15.22		129.82	
Charcoal			0.72	9.33		2.58		7.29	0.81				125		325	8.22		31.25	
Lime (CaO)			0.16	0.67		2.32	421.16		0.13		1.92		630		295	2.15		11.17	
Dolomite			0.11	0.52		28.5	269.81		0.18				1120		233	3.25		13.23	
$_{\rm Loam}$			0.41	21.60		17.3	23.87		$8.00\,$		3.2		38000		451	43.2		98.13	
Zeolite (natural) type MHZ			$0.11\,$	23.21		0.32	15.28		16.12		1.33		7950		342	5.52		32.22	
Zeolite (synthetic) type RBZ			0.15	32.37		$0.17\,$	21.12		4.31				8940		286	6.39		28.18	
Pinewood bark			0.18	0.44		0.62		0.55	0.15				153		112	16.23		19.30	
Peat			0.52	1.18		0.82		7.23	2.32		3.1		938		39.25	5.23		62.38	

Soil Pollution with Arsenic Versus the Concentration of Magnesium... 1487

Table 1

prepared as aqueous solutions. All the substances: the fertilizers, sodium arsenate and the neutralizing agents, once added to soil, they were thoroughly mixed with it and then transferred to pots. The soil used for maize trials had pH of 6.07 in $H₂O$ and 5.91 in KCl. Its hydrolytic acidity was 19.5 mmol \cdot kg⁻¹. This soil was moderately abundant in available phosphorus, potassium and magnesium. Cocksfoot and lupine were grown on soil of the reaction equal 5.75 in H_2O and 4.53 in KCl. Its hydrolytic acidity was 33.1 mmol \cdot kg⁻¹. Barley and swedes grew on soil of the reaction 5.53 in H₂O and 4.16 in KCl. Its hydrolytic acidity corresponded to 28.2 mmol \cdot kg⁻¹. In terms of their content of plant available phosphorus, potassium and magnesium, the soils were moderately abundant. The levels of carbon and nitrogen in all the test soils were comparable. The concentration of arsenic in the test soils was small and did not exceed the norms set for farmland soils. The highest concentration of As, 3.58 mg As \cdot kg⁻¹, was found in the soil under cocksfoot and yellow lupine. The smallest one, 2.21 mg As \cdot kg⁻¹, occurred in soil under barley and swedes. The soil used for trials on maize contained 2.71 mg $\text{As} \cdot \text{kg}^{-1}$. With respect to other trace elements, they were determined in very small amounts in all the soils. Having filled all the pots with the appropriate components, whose chemical composition can be found in Table 2, the test crops were sown. The plant stand per 1 pot was as follows: 10 maize plants, 8 cocksfoot plants, 8 yellow lupine plants, 15 spring barley plants and 5 swedes plants. Soil moisture in the plants was maintained at 60 % water capillary capacity. The plants were harvested during the technological maturity stage.

While harvesting the plants, plant material was sampled for laboratory analyses. The plant samples were fragmented, dried at 60 $^{\circ}$ C and ground. Having mineralized the samples, AAS method was used to determine their content of magnesium. The results were processed statistically with the Statistica software package [6], using single- and two-factor analysis of variance. Dependencies between the dose of arsenic and concentration of magnesium in plants were determined using Pearson's simple correlation.

Results and discussion

The effect of increasing contamination of soil with arsenic on the concentration of magnesium in the test crops was varied. The content of magnesium in the plant material sampled tended to be correlated with the level of soil contamination with arsenic. In addition, magnesium content depended on the plant's species, analyzed part and type of a neutralizing substance applied (Tables 3–7).

The pollution of soil with arsenic caused strong increase in the content of magnesium, both in aboveground parts and in roots of maize (Table 3). In a series without neutralizing agents, this increase equalled 61 % in above ground parts and 71 % in roots. The substances used to inactivate arsenic in soil significantly modified the concentration of magnesium. Regarding the aboveground parts, the level of magnesium rose by 30 % ($r = 0.792$) in the objects receiving loam to 200 % ($r = 0.976$) in the combinations treated with charcoal and 233 $\%$ (r = 0.975) in the pots which were enriched with natural zeolite. In maize roots, the increase in magnesium observed in the above series oscillated from 71 % ($r = 0.965$) in the objects without neutralizing additives to 225 % ($r = 0.921$) when charcoal had been added. The substances used to neutralize arsenic in soil affected the content of magnesium in both parts of maize. For example, charcoal added to soil produced a clear positive effect on the concentration of magnesium in aboveground parts of maize. The second best results were produced by compost and natural zeolite. Reverse relationships, especially when analyzing the impact of loam and compost, were observed in the case of maize roots.

Tabela 3

Magnesium concentration in aboveground parts and roots of maize (*Zea mays* L.) $[g \cdot kg^{-1} d.m.]$

a – type of neutralizing agents; b – arsenic contamination; significant for: $*$ p = 0.05, $*$ p = 0.01; r – correlation coefficient.

Soil contamination with arsenic also caused elevated concentrations of magnesium in aboveground parts and organs of cocksfoot (Table 4). In the aboveground parts this increase ranged from 15 to 36 % and in the roots – from 7 to 146 %. The highest rise in the concentration of magnesium in parts of cocksfoot plants was observed in the control series (without any neutralizing substances) and in the objects which received zeolite and charcoal. The substances used during the experiments in order to inactivate arsenic in soil caused more variation in the concentration of magnesium in roots than in aboveground parts of cocksfoot. Depending on the neutralizing agent applied, the average magnesium level was from 1.4 to 1.7 g Mg \cdot kg⁻¹ d.m. in aboveground parts and from 1.1 to 2.8 g Mg \cdot kg⁻¹ in roots.

Table 4

a – type of neutralizing agents; b – arsenic contamination; significant for: * p = 0.05, * p = 0.01; n.s. – differences non-significant; r – correlation coefficient.

The effect of soil pollution with arsenic on the concentration of magnesium in yellow lupine was much weaker than in maize or cocksfoot (Table 5). Regarding the aboveground parts of maize, soil contamination with arsenic raised their content of magnesium in most series. This increase was most evident in the objects treated with lime ($r = 0.834$), followed by those receiving compost ($r = 0.990$) and natural zeolite $(r = 0.930)$, reaching 71, 38 and 26 %, respectively. The aboveground parts of yellow lupine obtained from the control series $(r = 0.938)$ and the ones with synthetic zeolite $(r = 0.926)$ and charcoal $(r = 0.243)$ showed rather stable levels of magnesium and only very weakly dependent on the application of arsenic to soil. Changes in the concentration of magnesium in yellow lupine roots were less evident than in aboveground parts of this crop. In the above series, the average amount of magnesium in the roots of yellow lupine ranged from 1.1 to 1.5 g Mg \cdot kg⁻¹ d.m.

Table 5

Magnesium concentration in aboveground parts and roots of yellow lupine (*Lupinus luteus* L.) [g × kg–1 d.m.]

a – type of neutralizing agents; b – arsenic contamination; significant for: $*$ p = 0.05, $*$ p = 0.01; r – correlation coefficient.

The trials involving swedes showed that the simulated poisoning of soil with arsenic modified the concentration of magnesium in this crop, too, but the aboveground parts of swedes in the series treated with peat ($r = 0.930$), bark ($r = 0.933$) and synthetic zeolite $(r = 0.839)$ responded to the contamination by increasing the levels of Mg, whereas the roots of this crop, under analogous conditions, contained lower quantities of this nutrient (Table 6). Besides, the concentration of magnesium in swedes was found to be dependent on the inactivation substances applied. The largest concentrations of magnesium in the aboveground parts of swedes were found in the series treated with dolomite (on average, 2.6 g Mg \cdot kg⁻¹ d.m.) and in the roots in the series with pinewood bark (1.6 g Mg \cdot kg⁻¹ d.m.). In the other series, the magnesium content was 2.3–2.4 g Mg \cdot kg⁻¹ d.m. of leaves and 1.4–1.5 g Mg \cdot kg⁻¹ d.m. of roots.

Table 6

Magnesium concentration in aboveground parts and roots of swedes *(Brassica napus* L. var. *napobrassica* (L.) Rchb.) [g × kg–1 d.m.]

a – type of neutralizing agents; b – arsenic contamination; significant for: $*$ p = 0.05, $*$ p = 0.01; n.s. – differences non-significant; r – correlation coefficient.

With respect to spring barley, the highest magnesium content was discovered in roots, with lower amounts of this element occurring in grain and straw (Table 7). These concentrations were, on average, from 1.7–2.2 g $Mg \cdot kg^{-1}$ d.m. of roots and from 1.2 to 1.6 g Mg \cdot kg⁻¹ d.m. of grain and straw. The effect of higher doses of arsenic introduced to soil on magnesium levels in plant tissues was weaker in the case of barley grains than its straw or roots. Among the neutralizing substances tested, the strongest effect on the content of magnesium in barley plants was recorded in the series with dolomite and synthetic zeolite (Mg in roots) as well as the series treated with synthetic zeolite, pinewood bark or grain (Mg in barley straw). In the other series and in barley grain, modifications in the content of magnesium observed after the application of any of the neutralizing substances were small, not exceeding 10 %.

Scientific reports on the influence of arsenic on concentrations of microelements, including magnesium, in plants are scarce. The positive relationships we discovered between arsenic contamination of soil and content of magnesium in roots and aboveground parts of some of the test plants seem to confirm the results obtained by

Table 7

Magnesium concentration in grain, straw and roots of spring barley (*Hordeum vulgare* L.) [g × kg–1 d.m.]

a – type of neutralizing agents; b – arsenic contamination; significant for: * p = 0.05, ** p = 0.01; n.s. – differences non-significant; r – correlation coefficient.

Paivoke and Simola [7], who conducted a study on seed pea. It should be added, however, that the exact effect of arsenic contamination of soil on microelements in plant tissues depends on the species of a plant. In the present study, apart from higher magnesium concentrations in plant tissues under the effect of arsenic contamination of soil, we also noticed depressed levels of this element in leaves and roots of swedes. Gorlach and Gambus [8] as well as Kabata-Pendias [2] discovered that arsenic found in toxic concentrations in plants depressed their content of magnesium. Adding substances which buffer the influence of heavy metals on plants plays an important role in establishing the level of Mg in plant tissues [9–11]. This influence tends to be positive, as they raise the availability of magnesium, originating from the neutralizing substances themselves and from partly mineralized organic matter, eg from compost earth [12]. Zeolite produces a similar effect – it improves the amounts of plant available forms of magnesium in soil and their uptake by plants [13]. The references indicate that application of compost soil, charcoal and, in part, lime to soil raises the concentration of magnesium in particular organs of triticale, spring oilseed rape, maize [9, 11] and other crops [10]. In an experiment conducted by Ciecko et al [14], by introducing to soil compost earth, lime, bentonite and especially charcoal, it was possible to obtain higher content of magnesium in most parts of the test plants. Charcoal produced the strongest effect, as it raised Mg concentration from 20 % (oats grain), 78–81 % (oats straw and yellow lupine roots) up to 216 % in aboveground parts of radish. In contrast, depressed levels of magnesium were determined in roots of radish as a result of the application of bentonite and in aboveground parts of yellow lupine after the application of lime and bentonite. Analogous effects produced by lime were found by Hahn and Marschner [15] in their analyses of spruce roots. Regarding maize, lime and magnesium are most often determined to be antagonist to each other, which means that Mg concentration in plants is depressed when lime has been added to soil [14].

Conclusions

1. The concentration of magnesium in plants was in most cases positively correlated with the degree of soil contamination with arsenic. The content of magnesium in plant tissues also depended on the plant's species and test organ and on the type of a neutralizing agent applied to inactivate arsenic.

2. Positive correlation between soil contamination with arsenic and content of magnesium in plant tissues was established for roots and aboveground parts of maize, cocksfoot and yellow lupine, and for grain, straw and roots of spring barley. Changes in the content of magnesium were bigger in roots than in aboveground parts of plants, particularly in the case of spring barley. Swedes was the only plant which responded to arsenic pollution of soil by depressing the concentration of magnesium in both roots and aboveground parts.

3. The neutralizing agents used to inactivate arsenic produced the strongest effect on the concentration of magnesium in aboveground parts of maize and roots of cocksfoot. With the remaining plants, this effect was much weaker.

References

- [1] Han F.X., Su Y., Monts D.L., Plondinec M.J., Banin A. and Triplett G.E.: Naturwissenschaften 2003, **90**, 395–401.
- [2] Kabata-Pendias A. and Pendias H.: Biogeochemia pierwiastków śladowych. PWN, Warszawa 1999.
- [3] WHO. Arsenic and arsenic compounds. Environmental Health Criteria, 224. World Health Organization, Genewa 2001.
- [4] Jiang Q.Q. and Singh B.R.: Water Air Soil Pollut. 1994, **74**(3/4), 321–343.
- [5] Carbonell-Barrachina A.A., Aarabi M.A., DeLaune R.D., Gambrell R.P. and Patrick W.H.: Plant Soil 1998, **198**, 33–43.
- [6] StatSoft, Inc. STATISTICA (data analysis software system), version 7.1. www.statsoft.com, 2006.
- [7] Paivoke A.E.A. and Simola L.K.: Ecotoxicol. Environ. Safety 2001, **49**, 111–121.
- [8] Gorlach E. and Gambuś F.: Zesz. Probl. Post. Nauk Roln. 2000, 472(1), 287-295.
- [9] Ciećko Z., Wyszkowski M. and Żołnowski A.: Zesz. Probl. Post. Nauk. Roln. 1998, 455, 47-56.
- [10] Csizinszky A.A.: Proc. of the Florida State Horticult. Soc. 2000, **112**, 333–337.
- [11] Cieæko Z., Wyszkowski M., Krajewski W. and Zabielska J.: Sci. Total Environ. 2001, **281**(1–3), 37–45.
- [12] Eghball B., Wienhold B.J., Gilley J.E. and Eigenberg R.A.: J. Soil Water Conserv. Ankeny 2002, **57**(6), 470–473.
- [13] Abdi G., Khosh-Khui M. and Eshghi S.: Int. J. Agricult. Res. 2006, **1**(4), 384–389.
- [14] Cieæko Z., Kalembasa S., Wyszkowski M. and Rolka E.: Polish J. Environ. Stud. 2005, **14**(3), 365–370.
- [15] Hahn G. and Marschner H.: Plant Soil 1998, **199**(1), 23–27.

WP£YW ZANIECZYSZCZENIA GLEBY ARSENEM NA ZAWARTOŚĆ MAGNEZU W ROŚLINACH

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Abstrakt: Przeprowadzone badania wykonano w celu określenia wpływu zanieczyszczenia gleby arsenem na zawartość magnezu w roślinach. Zanieczyszczenie gleby arsenem w dawkach 10, 20, 30 i 40 mg As \cdot kg⁻¹ gleby testowano na łubinie żółtym, a w ilości: 25, 50, 75 i 100 mg As \cdot kg⁻¹ gleby na kukurydzy, kupkówce pospolitej, jeczmieniu jarym oraz brukwi pastewnej. Do neutralizacji oddziaływania kadmu na rośliny do gleby dodano: kompost, wapno, węgiel drzewny, ił i zeolit naturalny – w doświadczeniach z kukurydzą, te same materiały i zeolit syntetyczny – w badaniach z kupkówką i łubinem żółtym oraz torf, ił, korę sosnową, dolomit i zeolit syntetyczny w doświadczeniu z jęczmieniem i brukwią. Oddziaływanie wzrastającego zanieczyszczenia gleby arsenem na zawartość magnezu w poszczególnych organach testowanych roślin było zróżnicowane. Zawartość magnezu w roślinach była przeważnie dodatnio skorelowana z poziomem zanieczyszczenia gleby arsenem. Jego zawartość w roślinach zależała ponadto od gatunku rośliny, rozpatrywanego organu, jak również od rodzaju zastosowanej substancji do neutralizacji arsenu. Dodatnią korelację wykazano w odniesieniu do korzeni i części nadziemnych kukurydzy, kupkówki i łubinu żółtego oraz ziarna, słomy i korzeni jeczmienia jarego. Wieksze zmiany stwierdzono w korzeniach niż cześciach nadziemnych roślin, zwłaszcza w przypadku jęczmienia jarego. Jedynie części nadziemne i korzenie brukwi zareagowały spadkiem zawartości magnezu na zanieczyszczenie podłoża arsenem. Zastosowane dodatki neutralizujące najsilniej dodatnio działały na zawartość magnezu w częściach nadziemnych kukurydzy i korzeniach kupkówki. W przypadku pozostałych gatunków roślin ten wpływ był znacznie mniejszy.

Słowa kluczowe: zanieczyszczenie arsenem, substancje neutralizujące, rośliny, zawartość magnezu