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EFFECT OF SOIL CONTAMINATION WITH ARSENIC AND APPLICATION OF DIFFERENT SUBSTANCES ON THE MANGANESE CONTENT IN PLANTS

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Abstract

The aim of the study has been to determine the effect of some substances such as dolomite, loam, compost, pinewood bark, peat, lime, charcoal, natural and synthetic zeolite on reducing the impact of soil contamination with arsenic on the content of manganese in some plant species. The content of manganese in the test plants depended on the degree of soil contamination with arsenic, application of different substances as well as on the plant species and organ. Soil contamination with arsenic caused either an increase or a decrease in the content of manganese in plants depending on a plant species and organ. In the series without soil amending substances, in the arsenic contaminated objects the manganese content decreased in above-ground parts of cocksfoot and swede but increased in above-ground parts and roots of maize and yellow lupine, in roots of cocksfoot and swede and in straw and roots of spring barley. On the other hand, the highest rates of arsenic depressed the content of manganese in roots of cocksfoot, swede and spring barley. Addition of any of the aforementioned substances to contaminated soil changed the content of manganese in the plants. The most unambiguous effect of the different substances was determined in the case of above-ground parts of maize as well as above-ground parts and roots of cocksfoot, in which the manganese content fell down, and in roots of yellow lupine, grain and straw of spring barley, in which the content of manganese rose. Charcoal and loam caused the largest and synthetic zeolite led to the smallest changes in the content of manganese in plants.

Key words: arsenic contamination, substances application, plants, manganese content.

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WPŁYW ZANIECZYSZCZENIA GLEBY ARSENEM I APLIKACJI RÓŻNYCH SUBSTANCJI NA ZAWARTOŚĆ MANGANU W ROŚLINACH

Abstrakt

Celem badań było określenie oddziaływania dodatku do gleby wybranych substancji: dolomitu, iłu, kompostu, kory sosnowej, torfu, wapna, węgla drzewnego, zeolitu naturalnego i zeolitu syntetycznego na ograniczenie wpływu zanieczyszczenia gleby arsenem i zawartość manganu w wybranych roślinach. Zawartość manganu w badanych roślinach zależała od poziomu zanieczyszczenia gleby arsenem, aplikacji substancji oraz od gatunku i organu roślin. Zanieczyszczenie gleby arsenem powodowało zwiększenie lub zmniejszenie zawartości manganu w roślinach, w zależności od ich gatunku i organu. W serii bez dodatków, w obiektach zanieczyszczonych arsenem, odnotowano zmniejszenie zawartości manganu w częściach nadziemnych kupkówki i brukwi oraz zwiększenie jego zawartości w częściach nadziemnych oraz korzeniach kukurydzy i łubinu żółtego, w korzeniach kupkówki pospolitej i brukwi pastewnej, a także w słomie i korzeniach jęczmienia jarego. Jednakże najwyższe dawki arsenu wywołały zmniejszenie zawartości manganu także w korzeniach kupkówki, brukwi i jęczmienia jarego. Dodatek do gleby różnych substancji spowodował zmiany w zawartości manganu w badanych roślinach. Ich najbardziej jednoznaczny wpływ stwierdzono w częściach nadziemnych kukurydzy oraz w częściach nadziemnych i korzeniach kupkówki, w których następowało, na ogół, zmniejszenie, oraz w korzeniach łubinu żółtego, ziarnie i słomie jęczmienia jarego, gdzie wykazano zwiększenie zawartości manganu. Węgiel drzewny i ił powodowały największe zmiany w zawartości manganu w roślinach, a zeolit syntetyczny najmniejsze.

Słowa kluczowe: zanieczyszczenie arsenem, aplikacja substancji, rośliny, zawartość manganu.

INTRODUCTION

Air emission is one of the major sources of arsenic in soil, water and plants. Arsenic accumulation occurs via dry and wet deposition, i.e. with the participation of atmospheric precipitations and gravitational forces (Hławiczka 1998). Poland is not seriously threatened by environmental pollution with arsenic. Moreover, the emission of noxious elements to the atmosphere, including arsenic, has been decreasing in the last years. However, there are millions of people worldwide who are at risk of contracting illnesses caused by the toxic effect of arsenic (Han et al. 2003). The response of a human organism to arsenic depends on the amount of the element, type of contact, duration of the exposure, sources and chemical form of arsenic. At the third oxidation level, this element is 60-fold more toxic than at its fifth oxidation level. In turn, mineral forms of arsenic are up to 100-fold more harmful than organic ones. Also, the way and duration of the contact of arsenic with a human body have a large influence on its impact (ATSDR 2000, Jain, Ali 2000, Caussy 2003). According to Han et al. (2003), in 2000 a potential load of arsenic introduced to arable soils by man's activity was 283 kg As km^{-2}, which was 31-fold more than in 1990. The same authors estimate that one kg of the surface layer of soil (10 cm) potentially receives an average 2.18 mg As every year. Arsenic is highly vulnerable to redox conditions. Its presence and mobility in the environment largely depend on interactions between several other biogeochemical conditions, such as pH, microbial activity, ionic relations as well as the presence of loamy minerals or organic substance (Lipiński 2000, Warner 2003, Karczewska et. al. 2005). Such factors, which can be modified by natural processes as well as human activity, can largely affect the processes of absorption and desorption or dissolution and precipitation, which in turn modify the mobility of arsenic in the environment (Warner 2003) and the effect arsenic produces on plants, including their ability to uptake macro- and microelements. Thus, effective methods are being searched for to reduce the effect of this metal on soil properties and plants.

The present study has been conducted to determine the effect of adding to soil certain substances, such as dolomite, loam, compost, pinewood bark, peat, lime, charcoal, natural zeolite and synthetic zeolite, on reducing the influence of soil pollution with arsenic on the content of manganese in several plant species.

MATERIAL AND METHODS

The study consisted of a pot experiment conducted in a greenhouse of the University of Warmia and Mazury in Olsztyn. The pot trials were established on three soils similar in their physicochemical properties (during 4 years), all collected from the humus layer of typical Eutric Cambisols soil, characterised by the grain-size distribution of loamy sand. They were acidic or slightly acidic in reaction, moderately abundant in available phosphorus and potassium, moderately or poorly abundant in available magnesium. The content of arsenic and other trace elements was low and did not exceed the threshold levels set for lands used for agricultural purposes (*Ordinance of the Ministry for Environment* 2002). Out tests on the effect of soil contamination with arsenic added to soil in the doses of 10, 20, 30 and 40 mg As kg^{-1} of soil were carried out on cv. Juno yellow lupine (*Lupinus luteus* L.), and these which included 25, 50, 75 and 100 mg As kg^{-1} of soil involved cv. Scandia maize (*Zea mays* L.) cv. Nawra cocksfoot (*Dactylis glomerata* L.), cv. Ortega spring barley (*Horendum vulgare* L.) and cv. Sara swede (*Brassica napus* var. *napobrassica*). In order to reduce the influence of arsenic on the plants, the soils were enriched with the following substances: lime, natural zeolite, charcoal, loam and compost in tests on maize; lime, natural zeolite, charcoal, loam, compost and synthetic zeolite in tests on cocksfoot and yellow lupine; peat, pinewood bark, loam, dolomite and synthetic zeolite in tests on spring barley and swede. Both zeolites were relatively rich in manganese; also loam contained higher amounts of this element. Peat, pinewood bark, dolomite and calcium oxide had little manganese. The substances were added to soil in the amounts equal 3% in relation to the soil mass in a pot (9 kg) whereas lime and dolomite were introduced in the quantities corresponding to 1 hydrolytic acidity (Hh). In addition, a control series of tests was run (without any extra substances added to soil). The test soils were enriched with NPK fertilizers added in rates adjusted to fertilization requirements of particular crops. Arsenic was added to soil as sodium arsenate, nitrogen was introduced as urea, phosphorus as triple superphosphate and potassium as potassium salt, with all these compounds being applied as aqueous solutions. Having prepared the soils, the plants were sown in pots. After their emergence, the following stands were left per pot: 10 maize plants, 8 cocksfoot plants, 9 yellow lupine plants, 15 spring barley plants and 3 swede plants. The vegetative pot experiments were performed in 3 replications. During the vegetative growth of the plants, soil moisture content was maintained at 60% field water capacity. The plants were harvested at the technological maturity phase, after which the plant material was sampled for laboratory analysis.

The plant material was fragmented, dried at 60°C and ground. The content of manganese was determined by the atomic absorption spectrophotometry method (OSTROWSKA et al. 1991). The results underwent statistical processing (two-factorial analysis of ANOVA variance) using the software package Statistica (STATSOFT, INC. 2007). Additionally, Pearson's simple correlation coefficients were computed between the rates of arsenic and the content of manganese in the plant organs.

RESULTS AND DISCUSSION

The content of manganese in the plants depended on the degree of soil contamination with arsenic, application of the additional substances as well as the species and organs of plants (Table 1). Soil contamination with arsenic resulted in an increase or decrease in the concentration of manganese in plants, depending on a plant species and organ (Table 1). In the series without any substances added to soil, the content of manganese decreased in above-ground parts of cocksfoot and swede but increased in above-ground parts and roots of maize and yellow lupine, in roots of cocksfoot and swede and in straw and roots of spring barley in all the objects polluted with arsenic. The decrease in the concentration of manganese in above-ground organs of cocksfoot and swede was on a similar level and equalled, respectively, 23% (r=-0.847) and 21% (r=-0.947). Soil pollution with arsenic raised the content of manganese the highest in spring barley straw. The stimulating effect was the weakest in above-ground parts of maize and yellow lupine. The increase in the manganese content in roots was higher than in above-

Table 1

Effect of arsenic on manganese content (Mn) in plants in a series without additions (mg kg^{-1} d.m.)

Arsenic doses	Plant					
	yellow lupine (*Lupinus luteus* L.)	maize (*Zea mays* L.)	cocksfoot (*Dactylis glomerata* L.)	swede (*Brassica napus* L. var. *napobrassica* L. Rchb.)	spring barley (*Hordeum vulgare* L.)	
	Above-ground parts				grain	straw
0	65.56	79.80	336.50	156.40	48.96	110.25
I	67.11	84.50	275.60	138.25	48.91	158.95
II	67.67	84.20	266.00	135.70	48.76	171.75
III	71.11	83.20	263.70	131.00	48.06	174.75
IV	72.45	83.40	254.40	123.05	47.11	176.60
Average	68.78	83.02	279.24	136.88	48.36	158.46
r	0.975**	0.496	-0.847**	-0.947**	-0.915**	0.844**
LSD	3.76**	3.62**	13.72**	8.93**	n.s.	11.82**
Roots						
0	171.12	70.50	185.00	57.75	160.48	
I	172.29	86.25	197.55	62.35	162.26	
II	188.12	85.40	221.15	64.65	192.71	
III	212.21	91.50	248.35	71.10	189.32	
IV	n.a.	98.75	198.25	60.25	159.71	
Average	185.94	86.48	210.06	63.22	172.90	
r	0.937**	0.939**	0.488	0.427	0.243	
LSD	5.03**	4.51**	12.34**	3.58**	10.22**	

Arsenic doses:
yellow lupine: I – 10; II – 20: III – 30 and IV– 40 mg As kg^{-1} of soil;
other plants: I – 25; II – 50: III – 75 and IV – 100 mg As kg^{-1} of soil;
Significant for: * p=0.05, ** p=0.01; n.s. – differences non-significant;
r – correlation coefficient;
n.a. – not analysed because of an insufficient amount of plant material

ground parts of maize and yellow lupine. Under the effect of arsenic contamination, the content of manganese in maize roots increased by 40% (r=0.939) and in yellow lupine roots it rose by 24% (r=0.937). The highest increase in the accumulation of manganese in the arsenic contaminated treatments occurred in spring barley straw where it reached 60% (r=0.844).

Increased levels of manganese were also found in roots of cocksfoot and swede up to the contamination rate of 50 mg As kg^{-1} of soil and in spring barley roots but only up to the dose of 75 mg As kg^{-1} of soil. The highest rates of arsenic (100 mg As kg^{-1} of soil) caused depressed concentrations of manganese in the above organs of these plants.

The relevant literature contains very few publications which deal with the effect of arsenic contamination of soil on the content of manganese in plants. According to Päivöke and Simola (2001), under the effect of arsenic the content of manganese in plants declines, which has been partly confirmed in the authors' own research. Shaibur et al. (2008) found lower levels of manganese in shoots and roots of barley growing on a substratum contaminated with arsenic. In our research, the effect of arsenic was strongly dependent on the species and organ of a plant, although the dominant correlation was that between an increasing content of manganese in plants growing on increasingly contaminated objects.

Introduction of different substances to soil caused changes in the content of manganese in the analysed plants (Table 2). The least ambiguous effect of these substances occurred in above-ground parts of maize and in above-ground parts and roots of cocksfoot, where manganese tended to decline, as well as in roots of yellow lupine or grain and straw of spring barley, where more manganese was determined. The negative impact of the different substances was stronger in above-ground parts than in roots of maize. As for cocksfoot, a reverse tendency was revealed – modifications in the manganese content were larger in roots than in above-ground organs. The concentration of manganese in maize above-ground organs was depressed on average from 33-36% (lime, natural zeolite, compost) to 49-50% (loam, charcoal). In roots of maize, the negative effect on manganese occurred only when charcoal (34%) and natural zeolite (23%) had been applied. An analogous negative effect of compost and lime on the content of manganese in cocksfoot roots (46% less manganese) was larger that that produced by charcoal (41%), loam (33%) and natural zeolite (16%). In the above-ground parts of this plant, such an effect was evidently weaker. Loam and compost produced the strongest effect on roots of yellow lupine, although the other substances also favoured the accumulation of manganese in roots of this plant. In contrast, above-ground parts of yellow lupine, like roots of swede, were only slightly affected by the additional substances, except for natural zeolite, which depressed the content of manganese in above-ground organs of yellow lupine. Synthetic zeolite, dolomite and loam in particular depressed the content of manganese in above-ground parts of swede, unlike peat and pinewood bark. All the substances increased the content of manganese in grain and straw of barley. Peat and synthetic zeolite, in addition to the above, also raised the levels of this element in spring barley roots. There were only two substances – pinewood bark and dolomite – which reduced, albeit very slightly, the content of manganese in roots of this plant. The

Table 2

Effect of different substances on manganese content (Mn) in plants –average from series (mg kg^{-1} d.m.)

Substances	Plant					
	yellow lupine (*Lupinus luteus* L.)	maize (*Zea mays* L.)	cocksfoot (*Dactylis glomerata* L.)	swede (*Brassica napus* L. var. *napobrassica* L. Rchb.)	spring barley (*Hordeum vulgare* L.)	
Aerial parts					grain	straw
Without additions	68.78	83.02	279.24	136.88	48.36	158.46
Charcoal	66.29	40.90	348.60	-	-	-
Natural zeolite	56.50	55.88	235.75	-	-	-
Synthetic zeolite	69.11	-	270.56	121.09	53.58	191.13
Loam	73.56	41.98	250.86	78.70	67.95	188.51
Compost	68.74	53.43	251.12	-	-	-
Lime	75.58	55.73	262.80	-	-	-
Peat	-	-	-	151.11	57.67	172.44
Bark	-	-	-	154.00	60.73	208.39
Dolomite	-	-	-	107.59	79.05	185.19
Average	68.37	55.16	271.40	124.90	61.22	184.02
LSD	3.24**	4.17**	20.05**	9.67**	n.s.	n.s.
Roots						
Without additions	185.94	86.48	210.06	63.22	172.90	
Charcoal	219.85	57.26	124.23	-	-	
Natural zeolite	197.71	66.30	175.52	-	-	
Synthetic zeolite	225.83	-	227.56	62.53	201.43	
Loam	238.23	86.66	141.29	59.21	180.69	
Compost	253.28	86.65	113.88	-	-	
Lime	188.95	94.24	114.03	-	-	
Peat	-	-	-	69.76	212.13	
Bark	-	-	-	60.55	150.73	
Dolomite	-	-	-	59.46	164.12	
Average	215.68	79.60	146.50	62.46	180.33	
LSD	6.37**	6.18**	38.80**	4.05**	13.77**	

Significant for: *p = 0.05, **p = 0.01; n.s. – differences non-significant strongest and positive influence on the content of manganese was produced by loam (41%) and dolomite (63%) in grain as well as pinewood bark (32%) in straw of spring barley.

The content of manganese in plants depends on its availability in soil, which in turn is affected by some properties of soil, such as sorptive characteristics, conditioned by the presence of organic matter in soil and soil acidity. These soil properties can be modified by adding to soil organic substance and lime, which affects the availability of manganese and other nutrients taken up by plants. Mongia et al. (1998) found out that the liming of acidic soil caused lower levels of manganese in rice grain and straw. Analogous effects in other crops were reported by Andersson and Siman (1991). The results provided by Guo et al. (2007) implied that a change in soil pH led to a depressed content of manganese in barley roots and leaves. Analogous relationships were determined in roots of plants by Hahn and Marschner (1998) after applying dolomite lime to soil. Thus, the uptake of manganese by plants depends on both soil acidity and its sorptive capacity. A study carried out by Cummings and Xie (1995) shows that higher soil reaction causes a decline in the soil's content of bioavailable forms of manganese and, consequently, leads to less Mn in crops. These authors did not find out any positive effect produced by dolomite lime on the content of water soluble forms of manganese in soil, although enrichment of soil with bird manure was positively correlated with their content. According to Uyanoz et al. (2006), introduction of organic substance to soil leads to higher concentrations of manganese in plants, with the actual effect being dependent on the type of organic matter used, which can be given in the following decreasing order: municipal sewage > bird manure > farmyard manure > compost. Our results partly confirm the above reports.

CONCLUSIONS

1. The content of manganese in the test plants depended on the degree of soil contamination with arsenic, application of different substances as well as the species and organs of plants. Soil contamination with arsenic caused either an increase or a decrease in the content of manganese in crops, depending on their species and organs.

2. In the series without any additional substances, in the arsenic contaminated treatments, a decreased content of manganese was found in above-ground parts of cocksfoot and swede, whereas the concentration of this element in above-ground parts and roots of maize and yellow lupine, in roots of cocksfoot and swede and in straw and roots of spring barley increased. Nevertheless, the highest arsenic rates caused a decrease in the content of manganese in roots of cocksfoot, swede and spring barley.

3. Soil pollution with arsenic caused the largest increase in the content of manganese in straw of spring barley; the weakest effect of this factor occurred in above-ground parts of maize and yellow lupine.

4. Enrichment of soil with different substances caused changes in the content of manganese in the test plants. The least ambiguous effect of the various substances added to soil was determined for above-ground parts of maize and above-ground parts and roots of cocksfoot, where the manganese content tended to decline, as well as in roots of yellow lupine, grain and straw of spring barley, where more manganese was determined.

5. Charcoal and loam caused the largest and synthetic zeolite the smallest changes in the content of manganese in plants.

REFERENCES

ANDERSSON A., SIMAN G. 1991. *Levels of Cd and some other trace elements in soils and crops as influenced by lime and fertilizer level*. Acta Agr. Scand., 41(1): 3-11.

ATSDR 2000. *Toxicological profile for arsenic*. U.S. Department of Health and Human Services, Public Health Service, Atlanta GA.

CAUSSY D. 2003. *Case studies of the impact of understanding bioavability: arsenic*. Ecotox. Environ. Safe., 56: 164-173.

CUMMINGS G.A., XIE H.S. 1995. *Effect of soil pH and nitrogen source on the nutrient status in peach*. II. *Micronutrients.* J. Plant Nutr., 18(3): 553-562.

GUO T.R., ZHOU M.X., WU F.B., CHEN J.X. 2007. *Influence of aluminum and cadmium stresses on mineral nutrition and root exudates in two barley cultivars*. Pedosphere, 17(4): 505--512.

HAHN G., MARSCHNER H. 1998. *Cation concentrations of short roots of Norway spruce as affected by acid irrigation and liming*. Plant Soil, 199(1): 23-27.

HAN F.X., SU Y., MONTS D.L., PLONDINEC M.J., BANIN A., TRIPLETT G.E. 2003. *Assesment of global industrial-age anthropogenic arsenic contamination*. Naturwissenschaften, 90: 395-401.

HŁAWICZKA S. 1998. *Ocena emisji metali ciężkich do powietrza z obszaru Polski.* Cz. II. *Emisje w latach 1980-1995. [Evaluation of the emission of heavy metals to air in Poland.* Part II. *Emission in 1980-1995].* Arch. Ochr. Środ., 4: 91-108. (in Polish)

JAIN C.K., ALI I. 2000. *Arsenic: occurrence, toxicity and speciation techniques*. Water Res., 34 (17): 4304-4312.

KARCZEWSKA A., BOGDA A., SZULC A., KRAJEWSKI J., GAŁKA B. 2005. *Zanieczyszczenie arsenem gleb i osadów dennych strumieni w rejonie polimetalicznego złoża Żeleźniak w Górach Kaczawskich. [Arsenic pollution of soils and bottom sediments in streams near a polymetal source called Żeleźniak in the Kaczawskie Mountains].* J. Elementol., 10(3)/2: 747--755. (in Polish)

LIPIŃSKI W. 2000. *Czynniki kształtujące występowanie arsenu i rtęci w glebach użytków rolnych Lubelszczyzny. [Factors shaping the presence of arsenie and mercury in soils of agricultural land in the region of Lubelszczyzna].* J. Elementol., 5(1): 37-43. (in Polish)

MONGIA A.D., SINGH N.T., MANDAL L.N., GUHA A. 1998. *Effect of liming, superphosphate and rock phosphate application to rice on the yield and uptake of nutrients on acid sulphate soils*. J. Ind. Soc. Soil Sci., 46(1): 61-66.

Ordinance of the Polish Ministry for Environment of 9th September 2002. [*Rozporządzenie Ministra Środowiska z 9 września 2002 r. w sprawie standardów jakości gleby oraz standardów jakości ziemi*]. Dz.U. Nr 165, poz. 1359. (in Polish)

OSTROWSKA A., GAWLIŃSKI S., SZCZUBIAŁKA Z. 1991. *Metody analizy i oceny właściwości gleb i roślin. Katalog. [Methods of analysis and evaluation of properties of soi land plants. A catalogue].* Inst. Ochr. Środ., Warszawa, ss. 334. (in Polish)

PÄIVÖKE A.E.A., SIMOLA L.K. 2001. *Arsenate toxicity to Pisum sativum: Mineral nutrients, chlorophyll content, and phytase activity*. Ecotox. Environ. Safe., 49: 111-121.

SHAIBUR M.R., KITAJIMA N., SUGAWARA R. KONDO T., HUQ S.M.I., KAWAI S. 2008. *Physiological and mineralogical properties of arsenic-induced chlorosis in barley seedlings grown hydroponically*. J. Plant Nutr., 31(2): 333-353.

STATSOFT, INC. 2007. *STATISTICA (data analysis software system), version 8.0*. www.statsoft.com.

UYANOZ R., CETIN U., KARAARSLAN E. 2006. *Effect of organic materials on yields and nutrient accumulation of wheat*. J. Plant Nutr., 29(5): 959-974.

WARNER S.D. 2003. *Distinguishing natural and anthropogenic sources of arsenic: Implications for site characterization*. In: U.S. EPA Workshop on Managing Arsenic Risks to the Environment: Characterization of Waste, Chemistry, and Treatment and Disposal, U.S. Environmental Protection Agency, Denver, http://www.epa.gov/nrmrl/pubs/625r03010/625r03010.pdf: 38.