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EFFECTS OF LIME AND PEAT ON HEAVY METAL UPTAKE BY PLANTS FROM SOILS CONTAMINATED BY AN EMISSION OF A COPPER SMELTER *

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Fumes emitted by a stack of a copper smelter contained mainly galena (PbS), some oxides (PbO, CuO, ZnO, SO_2) and hydrocarbon compounds formed as products of coal conversion while smelting process [7]. Fugitive dust blown onto soil surrounding a smelter was accumulated in a thin top layer (0–3 cm depth). Heavy metals were slightly mobile and slightly washed down from that layer into a deeper soil horizon. A high concentration of trace metals, especialy of Cu and Pb, a high acidity of the top soil and a presence of bituminous-like substances are important factors in deterioration of soils.

A beneficial effect of an addition of peat and (or) carbonates in suppressing the uptake of toxic amounts of heavy metals by various crops was reported by several authors. However, the results were not uniform and showed a variable behaviour of heavy metals under various pH and other soil factors.

MATERIALS AND METHODS

The greenhouse experiments were conducted with two surface soils (0–3 cm depth) sampled at 1.0 and 2.5 km from the copper smelter in Głogów, Poland. The sample at 1.0 km was a light sand of pH 4.6 and 2.5 km sample was a silty loam of pH 5.4. Information about the soils and heavy metal contents are given in Table 1. Five replicates of each treatment with pot contained 1 kg of soil were prepared. The following treatments were applied:

1 — blank sandy soil,

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Table 1

Some properties of soil samples

Soil	Downwind distance Km	Mechanical fractions µ		Organic matter %	pH in 1 N KCl^x		Hydrolytic acidity me/100 g	Heavy metals			
		< 2	< 20		initial	after exp.		Cu	Pb	Zn	Cd
		%						ppm			
Sandy soil, brown type	1.0	3	7	0.4	4.6	4.9	3.08	830	325	100	2.5
Loamy soil, brown type	2.5	9	18	0.8	5.4	4.9	2.78	171	98	95	1.5

^{x} Value for control treatment. A final pH after all carbonate treatment was 6.2.

2 — soil with 2.13 g $CaCO_3$ (equal to 1.5 times hydrolytic acidity),

3 — soil with 1.15 g $CaCO_3$ (equal to 0.75 ha) and 0.96 g $MgCO_3$ (equal to 0.75 ha),

4 — soil with 1.15 g $CaCO_3$ (equal to 1 ha) and 0.65 g $MgCO_3$ (equal to 0.5 ha),

5 — 3% peat air dry basis,

6 — peat and $CaCO_3$ as in treatment 2,

7 — peat and $CaCO_3$ and $MgCO_3$ as in treatment 3,

8 — peat and $CaCO_3$ and $MgCO_3$ as in treatment 4.

The loamy soil received the same treatments except the carbonates were adjusted for the different acidity e.g. 1.5 HA was equal to 2.08 g $CaCO_3$ and 0.75 HA was equal to 0.87 g $MgCO_3$.

The greenhouse experiment was done in the 1976 and 1977 seasons using succesive crops of spinach (*Spinacia oleracea* L.), buckwheat (*Fagopyrum esculentum* Much.), and two crops of horsebean (*Vicia faba minor* L.).

Plants were harvested at a blooming stage. Samples were washed in deionized water prior to chemical analyses. Total contents of heavy metals in soils were determined after digestion with a mixture of acids (H_2F_2, $HClO_4$, HCl). The same acid mixture was use for plant material after ignition in a muffle at 450°C. Chemical analyses were made by AAS flame method directly from a solution or after a concentration into an ogranic phase. Content of sulfur was determed by X-ray fluorescence.

RESULTS AND DISCUSSION

Harmful effects of a high soil concentrations of metals emitted by copper smelters on a growth of plants has been reported by several authors [1, 3, 7, 9]. Growth of all plants on the blank soils without any amendment was very poor and spinach on sandy soil did not produce any crop. Buckwheat was less tolerant to the contamination than horsebean but both plants were chlorotic and stunted. Roots of those plants

Table 2

Some major elements in horsebean grown on amended soils
/percent air dry weight/
/arithmetic mean of five replicates and treatments/

Soil and treatment	Ca		Mg		K		S
	I	II	I	II	I	II	I
Sandy soils	0.56	0.50	2.8	0.3	1.8	1.5	0.37
Soil with peat	0.91	1.00	2.5	0.3	1.2	0.9	0.30
Soil with carbonates	0.92	1.00	3.4	0.3	1.1	0.9	0.41
Soil with carbonates and peat	0.88	1.10	3.0	0.3	1.0	0.9	0.23
Loamy soil	1.31	1.10	3.4	0.3	2.8	1.6	0.31
Soil with peat	1.26	1.20	3.3	0.3	2.5	1.6	0.27
Soil with carbonates	1.29	1.40	5.3	0.4	2.4	1.7	0.23
Soil with carbonates and peat	1.45	1.50	4.9	0.4	2.3	1.6	0.24

I, II - crops of 1976 and 1977

were stubby with a very limited growth. The effect of each treatment on plant growth was spectacular. In all the cases an addition of peat with carbonates together always gave the best results.

The chemical composition of plants grown on contaminated soils with and without amendment showed a great changes, but there were consistent for each plant and soil. There was no visible influence of soil treatments on a content of major elements (Table 2), but changes in heavy metal contents of plants were large (Fig. and 2). The highest content of trace metals was observed in buckwheat grown on sandy soil without any treatment: 1000 ppm Cu, 400 ppm Zn, 100 ppm Pb and

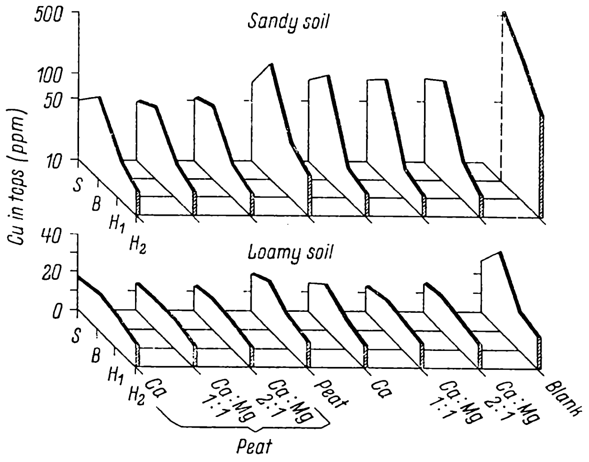


Fig. 1. Influence of soil treatment on copper uptake by plants
S — spinach, B — buckwheat, H_1 and H_2 — horesebean, 1976 and 1977 crops respectively

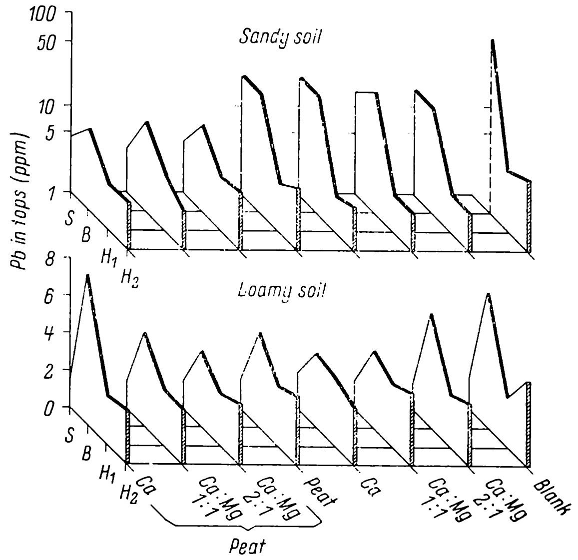


Fig. 2. Influence of soil treatment on lead uptake by plants
explanation see Fig. 1

Table 3

Some heavy metals in various plants as influenced by amendments of polluted soils
/ppm air dry weight/
/arithmetic mean of five replicates and treatments/

Plant	Treatment	Sandy soil				Loamy soil			
		Cd	Zn	Mn	Fe	Cd	Zn	Mn	Fe
Spinach	polluted soil	no yield				1.2	360	176	126
	soil with peat	0.5	200	168	330	1.2	380	90	56
	soil with carbonates	2.1	73	386	280	0.9	371	70	106
	soil with carbonates and peat	0.9	136	49	130	1.1	320	56	54
Buckwheat	polluted soil	2.5	400	260	950	2.1	260	122	324
	soil with peat	1.5	310	380	276	1.5	230	88	152
	soil with carbonates	1.1	160	508	161	1.0	140	69	374
	soil with carbonates and peat	0.8	133	39	104	1.0	140	56	176
Horsebean 1976	polluted soil	2.3	225	325	179	0.4	181	322	104
	soil with peat	0.3	168	206	81	0.7	181	259	103
	soil with carbonates	0.2	70	133	75	0.4	147	184	109
	soil with carbonates and peat	0.3	89	48	86	0.3	125	176	101
Horsebean 1977	polluted soil	0.8	208	364	160	0.6	110	330	90
	soil with peat	0.2	115	239	104	0.4	112	281	91
	soil with carbonates	0.1	59	142	72	0.3	69	136	83
	soil with carbonates and peat	0.1	69	77	91	0.3	68	124	86

2.5 ppm Cd (Table 3). The concentration of those metals in other plants grown on both sandy and loamy soils was much lower.

Relative suppression of heavy metal uptake indicated that an effect of the soil amendements were more effective for Cu, Cd and Fe than for Pb, Mn and Zn on sandy soil, but on the loamy soil the effects were much less (Table 4). However it is possible that some heavy metals were accumulated by plant roots to a much higher degree than by tops in this experiment. It is known that under certain conditions heavy metals, and especially lead, are stored in root tissues and not transported into the tops [4, 6, 7].

Table 4

Factor[x] of relative supressing of heavy metal uptake by plants from amended soils

Plant	Treatment	Cu	Pb	Cd	Zn	Mn	Fe
Sandy soil							
Buckwheat	peat	4.6	4.5	1.7	1.3	0.7	3.4
	carbonates[xx]	6.7	5.0	2.1	2.5	0.5	5.9
	peat and carbonates	13.5	10.0	3.1	3.0	7.0	9.1
Horsebean 1976	peat	8.8	1.6	7.7	1.3	1.6	2.2
	carbonates	17.7	1.9	10.0	3.2	2.4	2.4
	peat and carbonates	15.7	1.3	8.8	2.5	6.7	2.1
Horsebean 1977	peat	4.8	1.4	4.0	1.8	1.5	1.5
	carbonates	7.9	2.2	8.0	3.5	2.6	2.2
	peat and carbonates	7.9	1.8	8.0	3.0	4.7	1.7
Loamy soil							
Spinach	peat	1.4	1.0	1.0	0.9	1.9	2.3
	carbonates	1.9	1.0	1.3	0.9	2.5	1.3
	peat and carbonates	2.0	1.1	1.1	1.1	3.1	2.4
Buckwheat	peat	1.6	1.4	1.4	1.1	1.4	2.1
	carbonates	2.2	1.5	2.1	1.9	1.8	0.9
	peat and carbonates	2.5	1.3	2.1	1.8	2.2	1.8
Horsebean 1976	peat	1.2	0.8	0.6	1.0	1.2	1.0
	carbonates	1.3	0.8	1.0	1.3	1.8	1.0
	peat and carbonates	1.3	1.0	1.5	1.5	1.8	1.0
Horsebean 1977	peat	1.2	1.2	1.5	1.0	1.2	1.0
	carbonates	1.4	1.3	2.0	1.6	2.4	1.1
	peat and carbonates	1.6	1.4	2.0	1.6	2.7	1.1

[x] Factor is calculated as a ratio of heavy metal concentration in plants grown on polluted soils to those grown on amended soils

[xx] Average value for all carbonates treatments

Concentration of heavy metals in the natural soil solution was determined for each treatment at the termination of the experiment (Table 5). All the treatments depressed the content of heavy metals in the solution from the sandy soil. In loamy soil however, an increase in concentration of Cu, Pb, Mn and Fe was observed after carbonate addition (mainly $CaCo_3$).

Table 5

Chemical composition of natural soil solution after the experiment

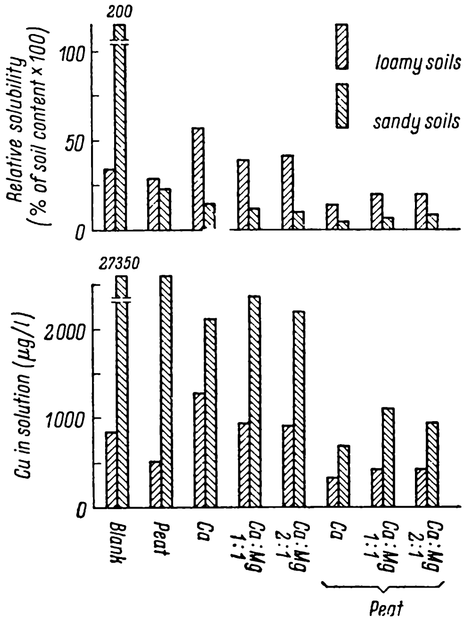
Soil and treatment	Cd	Zn	Mn	Fe	Ca	Mg	K
	ppb				ppm		
Sandy soil - control	70.51	13034	12400	n.d.	166	53.9	96.2
Sandy soil with:							
$CaCO_3$	8.00	390	5200	3500	330	18.8	12.3
$CaCO_3$ + $MgCO_3$ /1:1/	8.20	410	5328	5277	207	90.2	9.8
$CaCO_3$ + $MgCO_3$ /2:1/	5.90	384	4331	4577	194	63.8	10.9
Sandy soil + peat - control	18.29	2947	5061	4726	186	36.2	33.6
Sandy soil + peat with:							
$CaCO_3$	5.21	352	1042	124	438	27.1	7.8
$CaCO_3$ + $MgCO_3$ /1:1/	6.88	298	1537	212	264	87.2	8.3
$CaCO_3$ + $MgCO_3$ /2:1/	6.10	275	3720	3659	295	71.6	6.4
Loamy soil - control	5.32	470	11702	1108	102	19.2	28.4
Loamy soil with:							
$CaCO_3$	1.41	404	19817	4230	259	25.0	24.4
$CaCO_3$ + $MgCO_3$ /1:1/	5.10	144	10204	2168	161	57.5	23.0
$CaCO_3$ + $MgCO_3$ /2:1/	4.78	120	10510	2110	183	47.8	21.5
Loamy soil + peat - control	4.66	466	11957	4969	102	16.8	10.0
Loamy soil + peat with:							
$CaCO_3$	3.16	480	14399	831	133	13.3	7.4
$CaCO_3$ + $MgCO_3$ /1:1/	6.33	150	4114	22943	190	55.7	9.0
$CaCO_3$ + $MgCO_3$ /2:1/	4.84	137	9032	4943	154	33.2	8.6

The Cu concentration in the solution from sandy soil was above 27 000 ppb and decreased after a peat addition to 2600 ppb, after carbonate treatments — to 2200 ppb (average) and with peat and carbonates together — to 940 ppb. In loamy soil the changes of Cu concentration were as follows: soil — 800 ppb, soil + peat — 560 ppb, soil + carbonates 1040 ppb and soil + carbonates + peat — 417 ppb.

The relative mobility of Cu however, expressed as concentration in soil solution in percent of total content of soil, was higher for all treatments in the loamy soil (average 0,3$^{0}/_{0}$) than in the sandy soil

(0,15%). In the blank soils however, that proportion was different (Fig. 3).

The values obtained for a mobility of Pb (sandy soil — 0,009% and loamy soil — 0,03%) under various treatment were much lower than for Cu, but in general it was similar to the trend observed for Cu. The solubility of Cd, and Zn (average 0,12%) also showed a fairly stable behaviour of those elements under liming and amended soils with peat (Fig. 4). A liming and peat addition were much less effective in suppressing the solubility of Mn. The order of a mobility of heavy metals, in this experiment, based on their percentage solubility (given in parentheses) in soil solution is as follows:



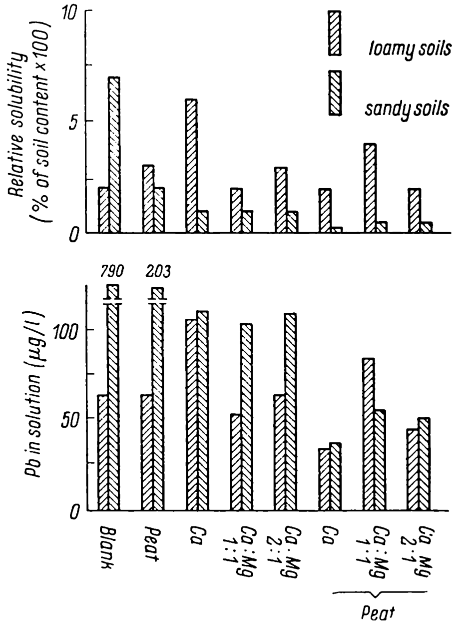


Fig. 3. Copper content of soil solution and its solubility as affected by various soil treatment

Fig. 4. Lead content of soil solution and its solubility as affected by various soil treatment

Mn (0,74)>Cu (0,22)>Cd (0,14)>Zn (0,1)>Pb (0,02)>Fe (0,01)

The suppressing effect of carbonates and peat on an uptake of trace metals was quite different for buckwheat and horsebean. A variable ratio of carbonates (e.g. Ca:Mg) was without any significant effect on bioavailability of the heavy metals. Peat added to the soils without carbonates suppressed heavy metal uptake only on sondy soil. The effect of soil pH and liming on Cu and Pb uptake by plants is variable and in certain environments does not suppress the bioavailability of those metals very much [2, 5, 8]. In this experiment however, carbonates, especially when applied together with peat on acid sandy soil, have suppressed the concentration of heavy metals in soil solution and in all crops. There were however no significant differences in the treatments on the loamy soil.

Relative suppression of heavy metal uptake showed that the effect of soil amendment was much higher for Cu, Cd and Fe than for Pb, Mn and Zn on sandy soil, while on loamy soil these values did not differ much for each metal (Table 3). It is possible however that metal accumulation by the roots was much higher and in another proportion than by the tops.

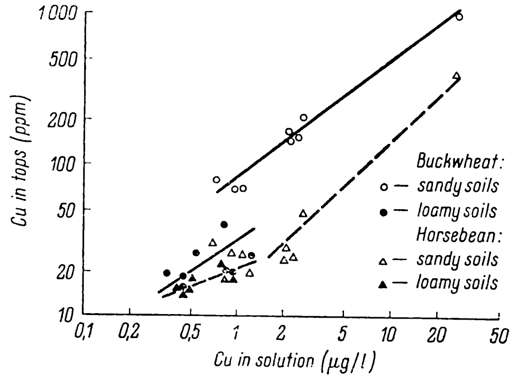


Fig. 5. Copper uptake by the tops of buckwheat and horsebean versus its concentration in soil solution

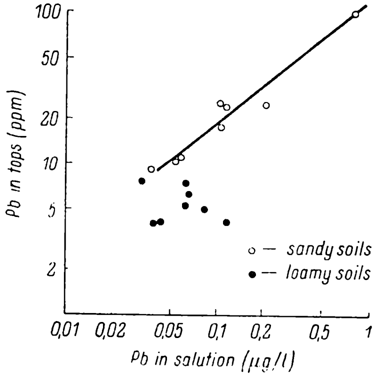


Fig. 6. Lead uptake by the tops of buckwheat versus its concentration in soil solution

The uptake of heavy metals by plants seems to be controlled mainly by their concentration in natural soil solution. This is affected by a large number of soil factors and also depended on plant species (Fig. 5 and 6). The results of the experiment showed that content of carbonates and organic matter are of a great importance. Effects of liming in suppressing the uptake of toxic amounts of heavy metals by plants is complex and depends on both the rooting medium and the plant tissues.

The benefitial influence of lime and peat on soils contaminanted with heavy metals depends on various soil factors and should be investigated for each kind of soils.

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REFERENCES

[1] Balicka N., Węgrzyn T., Varanka- M.: An impact of flay ash of a copper smelter on microorganisms in soil and plants (in Polish). Mat. Sesji Nauk. PAN Oddz. Wrocław, 8-9, 1974, 313-316.

[2] Gadde R. R., Laitinen H. A.: Study of the interaction of lead with corn root exudate. Envir. Letters 5, 1973, 91-102.

[3] Hutchinson T. C., Whitby L. M.: A study of air borne contamination of vegetation and soils by heavy metals from the Sudbury, Ontario copper--smelters. Trace Subst. Envir. Health 7, 1973, 179-183.

[4] Jones L. H., Jarvis S. C., Cowling D. W.: Lead uptake from soils by perennial ryegrass and its relation to the supply of an essentail elements. Plant a. Soil 38, 1973, 605-619.

[5] Kabata-Pendias A.: Heavy metal accumulation of plants grown on gangue slurries of the copper mine (in Polish). Rocz. Gleb. 28, 1977, 141-154.

[6] Kabata-Pendias A.: Influence of lead on chemical composition of grass (Bromus unioloides) (in Polish). Rocz. Nauk Roln. 102 Ser. A, 1977, 29-38.

[7] Kabata-Pendias A., Gondek B.: Bioavailability of heavy metals in vicinity of a copper smelter Trace Subst. Envir. Health 12, 1979.

[8] Lagerwerff J. V., Armiger W. H., Specht A. W.: Uptake of lead by alfalfa and corn from soil and air. Soil Sci. 115, 1973, 455-460.

[9] Roszyk E.: Contamination of soil and crops with Pb, Cu and Zn in the region of copper works (in Polish). Z. Probl. Post. Nauk Roln. 206, 1978, 65-67.

А. КАБАТА-ПЕНДИАС

ВЛИЯНИЕ ИЗВЕСТКОВАНИЯ И ВНЕСЕНИЯ ТОРФА НА УСВОЕНИЕ ТЯЖЕЛЫХ МЕТАЛЛОВ РАСТЕНИЯМИ ИЗ ПОЧВ ЗАГРЯЗНЕННЫХ ЭМИССИЕЙ МЕДЕПЛАВИЛЬНОГО ЗАВОДА

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Резюме

Две почвы отобранные вблизи медеплавильного завода в Глогове (табл. 1) были известкованы различными дозами карбонатов кальция и магния при их совместном внесении в количестве эквивалентном 1,5 гидролитической кислотности. Кроме того проводились опыты с прибавкой торфа в количестве 3% (в пересчете на сухое вещество торфа) к почвам контрольным и известкованным. Вегетационные (сосудные) опыты были проведены в период двух летних сезонов (1976 и 1977) со следующими выращиваемыми поочередно растениями: шпинат, гречиха и два урожая конских бобов.

Влияние прибавки карбонатов и торфа к почве на урожай и химический состав растений проявилось иначе на каждой из почвенных разновидностей. Не были обнаружены различия в действии карбонатов при изменении соотношения Ca:Mg. Содержание главных химических элементов тоже не подвергалось изменению (табл. 2). Однако концентрация микроэлементов, а особенно меди и свинца, показала существенную дифференцированность (табл. 3, график 1 и 2). Самые высокие концентрации металлов были обнаружены в гречихе выращиваемой на контрольной песчаной почве; они составляли: 1000 ppm Cu, 400 ppm Zn, 100 ppm Pb и 2,5 ppm Cd.

Прибавка карбонатов и торфа к песчаной почве снижала усвоение металлов растениями, но это влияние проявилось сильнее в отношении Cu и Cd. В суглинистой почве было отмечено значительно меньшее понижение усвоения микроэлементов (табл. 4).

Химической состав почвенных растворов после окончания опыта (табл. 5) показал, что под влиянием известкования песчаной почвы понизилась растворимость Cu и Pb, тогда как в суглинистой почве обнаружился рост их растворимости (график 3 и 4). Активность перехода микроэлементов из стабильной фазы в почвенный раствор, выражаемая процентной растворимостью по соотношению к содержанию в почве, представляется следующе:

$$Mn > Cu > Cd > Zn > Pb > Fe$$

Усвоение металлов растениями зависит непосредственно от их концентрации в почвенном растворе, а следовательно и от их растворимости (график 5 и 6). Названная зависимость находится однако под сильным влиянием разнообразных почвенных факторов, а также индивидуальных свойств растений. Поэтому влияние известкования и внесения торфа на снижение усвоения тяжелых металлов растениями следует всегда устанавливать для определенных почвенных условий и видов растений.

A. KABATA-PENDIAS

WPŁYW WAPNOWANIA I TORFOWANIA NA POBIERANIE METALI CIĘŻKICH PRZEZ ROŚLINY Z GLEB ZANIECZYSZCZONYCH EMISJĄ HUTY MIEDZI

Instytut Uprawy, Nawożenia i Gleboznawstwa w Puławach

Streszczenie

Dwie gleby pobrane w pobliżu huty miedzi w Głogowie (tab. 1) wapnowano różnymi dawkami węglanu wapnia i magnezu, wprowadzając oba składniki łącznie w ilościach odpowiadających 1,5 kwasowości hydrolitycznej. Ponadto założono serie doświadczenia z dodatkiem torfu w ilości 3% (w przeliczeniu na suchą masę torfu) do gleb kontrolnych oraz wapnowanych. Doświadczenie wazonowe prowadzono w okresie dwóch sezonów letnich (1976 i 1977) z następującymi kolejno roślinami: szpinak, gryka oraz dwa plony bobiku.

Wpływ dodatku węglanów i torfu do gleby na plon i skład chemiczny roślin

był odrębny dla każdego rodzaju gleby. Nie zaznaczyły się różnice w działaniu węglanów o zmiennej proporcji Ca:Mg. Zawartość głównych pierwiastków chemicznych w roślinach nie ulegała zmianie (tab. 2). Natomiast stężenie pierwiastków śladowych, a zwłaszcza miedzi i ołowiu, wykazywało istotne zróżnicowanie (tab. 3, rys. 1 i 2). Najwyższe stężenia metali wystąpiły w gryce rosnącej na kontrolnej glebie piaszczystej; wynosiły one 1000 ppm Cu, 400 ppm Zn, 100 ppm Pb i 2,5 ppm Cd.

Dodatek węglanów i torfu do gleby piaszczystej obniżył pobranie metali przez rośliny, ale wpływ ten zaznaczył się najsilniej w stosunku do Cu i Cd. W przypadku gleby gliniastej nastąpił znacznie mniejszy spadek pobrania metali śladowych (tab. 4).

Skład chemiczny roztworów glebowych po zakończeniu doświadczenia (tab. 5) wykazał, że pod wpływem wapnowania gleby piaszczystej obniżyła się rozpuszczalność Cu i Pb, podczas gdy w glebie gliniastej zaznaczył się wzrost ich rozpuszczalności (rys. 3 i 4). Aktywność przechodzenia pierwiastków śladowych z fazy stałej do roztworu glebowego, wyrażona procentową rozpuszczalnością w stosunku do zawartości w glebie, przedstawia się następująco:

$$\mathrm{Mn} > \mathrm{Cu} > \mathrm{Cd} > \mathrm{Zn} > \mathrm{Pb} > \mathrm{Fe}$$

Pobieranie metali przez rośliny jest bezpośrednio uzależnione od ich stężenia w roztworze glebowym, a więc również od ich rozpuszczalności (rys. 5 i 6). Wymieniona zależność pozostaje jednakże pod dużym wpływem różnych czynników glebowych oraz właściwości roślin. Dlatego wpływ wapnowania i torfowania na ograniczenie pobierania metali ciężkich przez rośliny należy ustalać zawsze dla określonych warunków glebowych i roślin.

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