INFLUENCE OF NATURAL AND ARTIFICIAL HUMIC ACIDS ON DECREASE OF Zn AND Cd TOXICITY FOR PEA PLANTS (*Pisum sativum* L.)

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Summary. This article presents a study on the effect of natural and artificial humic acids on zinc and cadmium toxicity for pea plants (*Pisum sativum* L.). The research was carried out in water cultures on the modified Knopp substrate. Toxic quantities of Zn and Cd were added to the substrate in the form of soluble nitrogen salts. Two natural humic acids were prepared from Luvisol and degraded chernozems. Artificial humic acids came from Aldrich company. Different influence of both natural and artificial humic acids point out to three mechanisms: (i) difference of cation exchange capacity and amounts of carboxilic and phenolic groups of all amendments; (ii) chemical properties of zinc and cadmium ions; (iii) ratio between amount of three types of humic acids and metal contents. Humic acids from Aldrich company were a factor determining zinc and cadmium activity for pea plants. Humic acids from degraded chernozem caused a decrease of cadmium activity of investigated plans.

Key words: humic acids, zinc and cadmium toxicity, pea plants

INTRODUCTION

Elevated mobility of toxic elements in the environment results in an increase of their accumulation in plants, which is a serious threat for living organisms [Spiak *et al.* 2000]. Organic matter greatly contributes to changes of particular forms of toxic elements in soils [Gunnela *et al.* 2007; Sosulski *et al.* 2007]. Those changes depend on environmental pH and chemical properties of the elements themselves [Stevenson 1994, Sparks 1995, Basta *et al.* 2001, Rogóż 2002, Usman *et al.* 2006]. According to Sposito [1989], reactivity of organic matter components depends on their multi-functionality, molecule charge and structural

flexibility. In the opinion of Evangelou *et al.* [1999] and Bradshaw [2000], bonds between organic matter and heavy metals may be formed on the basis of ionic exchange (outer-sphere complexes) and ligand or coordination bond exchange (inner-sphere complexes).

The aim of the present research was to evaluate the influence of artificial and natural humic acids on changes of cadmium and zinc ion toxicity for common pea plants (*Pisum sativum* L.).

MATERIAL AND METHODS

Aqueous cultures in which the experiments were carried out were set in plastic pots of 4 dm³ capacity on modified Knopp medium (not containing phosphate ions) [Brauner and Bukatsch 1987]. The basic medium contained the following salts:

$Ca(NO_3)_2$	1,0 g dm ⁻³	H_3BO_3	550 mg dm ⁻³
KNO ₃	0,25 g dm ⁻³	MnCl ₂	350 mg dm ⁻³
KCl	0,12 g dm ⁻³	$CuSO_4 \cdot 5H_2O$	50 mg dm ⁻³
$MgSO_4$ · $7H_2O$	0,25 g dm ⁻³	$ZnSO_4$ · $7H_2O$	50 mg dm ⁻³
2% C ₆ H ₅ FeO ₇ H ₂ O	$1 \text{ cm}^{3} \text{ dm}^{-3}$		-

Ions of toxic metals (zinc and cadmium) were added to the medium in the form of soluble nitrates (6 and 4-water molecule hydrates, respectively) at the amounts of 150 mg Zn dm⁻³ and 3 mg Cd dm⁻³. Three types of humic acids (h.a.) were used in the experiments: artificial preparation by Aldrich company and two natural ones extracted from lessive soil and chernozem degraded according to Konanowa [1968]. There were applied 200 mg dm⁻³ aliquots of humic acid preparations. In total, 12 treatments were created (Tab. 1, 3, 4), each in three replications. Abovementioned aqueous cultures were subjected to 2-week tests of reaction of studied plants towards the Zn²⁺ or Cd²⁺ ions in the solution on the background of applied humic acids.

After 14 days of common pea growth and development, harvest of plant biomass was made, separating aboveground parts from roots. Then, fresh matter of aboveground parts was weighed, roots were measured and, after drying, dry matter of aboveground parts and roots was weighed. After grinding of dried samples, their digestion in concentrated sulphuric acid with 30% H_2O_2 addition was performed [Ostrowska *et al.* 1991].

Directly after plant cutting, pH of particular solutions was measured by means of potentiometry. Concentrations of studied heavy metal ions in medium were determined using the AAS technique (atomic absorption spectrometry). AAS technique also served for evaluation of zinc and cadmium contents in plant samples. Measurement was carried out in digested plant solutions. Variance analysis of results was carried out applying Tukey's confidence intervals.

Changes of some parameters of humic preparations before and after the experiment were also recorded. Their sorption capacity (total and exchangeable) was measured. The sum of carboxilic and phenolic groups, and carboxilic groups alone was estimated; the amount of phenolic groups on their own was calculated by subtraction [Konanowa 1968] (Tab. 2).

RESULTS AND DISCUSSION

Influence of humic preparations on the presence of zinc and cadmium ions in medium

Significant changes were observed in the content of soluble forms of zinc and cadmium under the influence of natural and artificial humic preparations (Tab. 1). The greatest decrease of Zn^{2+} ion concentration in relation to treatment No. 5 (0 + Zn) was found in treatment No 6., i.e. at the presence of artificial humic preparation by Aldrich company, then in the treatment with humic acids extracted from degraded chernozem (treatment No. 8, Tab. 1). No general changes of Zn^{2+} ion content in the solution were recorded after the application of humic acids extracted from lessive soil (treatment No. 7). All three humic preparations caused a significant decrease of Cd^{2+} ions in the solution (Tab. 1, treatments No. 10–12) as compared to treatment No. 9 (0 + Cd), however, the greatest (6-fold) decrease of cadmium ions was recorded when the natural humic preparation extracted from degraded chernozem was used.

No.	Treatment	Cd mg · dm ⁻³	Zn mg · dm ⁻³	pH of solution	
1	0	0.00	0.01	5.3	
2	0 + h.a. from Aldrich	0.00	0.13	5.6	
3	0 + h.a. orthic luvisol	0.00	0.05	5.5	
4	0 + h.a. haplic phaeozem	0.00	0.06	5.9	
5	0 + Zn	0.03	62.50	5.0	
6	0 + Zn + h.a. from Aldrich	0.00	44.00	5.2	
7	0 + Zn + h.a. orthic luvisol	0.00	63.00	5.1	
8	0 + Zn + h.a. haplic phaeozem	0.01	59.50	5.5	
9	0 + Cd	0.96	0.16	5.5	
10	0 + Cd + h.a. from Aldrich	0.60	0.04	5.8	
11	0 + Cd + h.a. orthic luvisol	0.30	0.01	5.6	
12	0 + Cd + h.a. haplic phaeozem	0.16	0.01	6.0	
x		0.17	19.12		
	$LSD_{0.05}$	0.59	9.78		

Table 1. Content of zinc and cadmium in the solution

The changes of free zinc and cadmium ions in solution were caused by complexing effect of the organic compounds used towards heavy metals [Alloway 1990, McBride *et al.* 2000, Bradshaw 2000, Usman *et al.* 2006]. However, that effect varied for both types of ion and depended on the preparation applied. The artificial preparation (Aldrich) significantly decreased the amounts of free Zn^{2+} and Cd^{2+} ions, and the two natural humic preparations significantly decreased the content of free cadmium ions. The preparation extracted from chernozem decreased the amount of free zinc ions, but to a lesser extent than that produced by the Aldrich company. It should be stated that, in the case of free cadmium ions (treatments No. 9–12, Tab. 1), decrease of their level in solution was the resultant of humic acid action and changes of solution pH. The influence of pH on the change of free zinc ions was of lesser importance (Tab. 1). It seems that both metals were bonded to organic matter in different ways, but Zn + h.a. from Aldrich binding was more specific and probably of inner-sphere type [Evangelou *et al.* 1999, Shuman 1999], and cadmium showed obviously higher

	After investigation					Before investigation				
Treatment	Amount of functional group/1 g h.a.		Capacity/100 g of ash-free sub- stances		Amount of functional group/1 g h.a.			Capacity/100 g of ash-free substances		
	COOH + OH	СООН	НО	total	exchangeable	COOH + OH	СООН	НО	total	exchangeable
0 + h.a. from Aldrich	0.54 (0.34 [*])			54		0.88	0.17	0.71	88	17
0 + h.a. ortihic luvisol	2.97 (0.34 [*])	1.75 (2.1 [*])	1.22	297	175	5.0	3.85	1.15	500	385
0 + h.a. haplic phaeozem	4.27 (2.52 [*])	1.82 (2.99 [*])	2.45	427	185	6.79	4.81	1.98	679	481
0 + Zn h.a. from Aldrich	Determin sample –	Determination was made from very small sample – results exceed the h.a. from Ald- rich capacity								
0 + Zn + h.a. or- thic luvisol	3.02	1.72	1.3	302	177					
0 + Z + h.a. haplic phaeozem	4.11	1.76	2.35	411	176					
0 + Cd + h.a. from Aldrich	Results burdened with errors because of small sample									
0 + Cd + h.a. or- thic luvisol	0.56	0.93	0.33	56	28					
0 + Cd + h.a. hap- lic phaeozem	0.56	0.93	0.33	56	23					

Table 2. Changes of some properties of humic acids used

* reacted

affinity to all types of organic matter, which is consistent with the opinion of some authors [Gorlach and Gambuś 2000, Gambuś and Rak 2000]. However, all Cd h.a. bonds were non-specific and probably of outer-sphere type [Evangelou *et al.* 1999].

The above mechanisms of zinc and cadmium ion binding by natural and artificial humic preparations are indicated by the characteristics of some properties of humic acids applied in the experiment (Tab. 2). Those acids were characterized with varied sorption capacity before experiment setting. Total capacity of humic acids extracted from the soils was several times higher than of that of the humic acid purchased from Aldrich. At the same time it should be mentioned that humic acids from chernozem were characterized with higher total capacity as compared to humic acid from lessive soil. The results of determinations of sorption capacity for the analysed humic acids after the experiment completion indicate that, in the case of natural humic acid preparations in the variant with zinc, sorption capacity decreased to the determination limit for the method. Therefore, one can suppose that COOH and OH moieties were substituted with Zn²⁺ ions. In the case of the treatments with cadmium, natural humic acids were characterized with much lower selectivity. This is indicated by the determined amounts of COOH and OH groups. In the case of OH moieties, their amounts were similar to those in the initial humic acid samples. On a basis of the determined amounts of COOH moieties it can be supposed that hydrogen ion could be replaced by Cd²⁺ ions. The decrease of total capacity of natural humic acids in cadmium-amended treatments after experiment completion may be accounted for by the decrease of COOH moiety amount (Tab. 2).

In the treatments with Zn and Cd where h.a. from Aldrich were applied, the determinations were made using very small aliquots (Tab. 2) and thus the results are burdened with very high error (they exceeded the sorption capacity of h.a. from Aldrich), which points out to total affinity of functional groups of the preparation both to zinc and cadmium ions (Tab. 2).

Plant reaction towards zinc and cadmium under the influence of humic acids applied

An increase of fresh and dry matter of aboveground parts of common pea was found in treatments where both natural and artificial humic acids were used alone (treatments No. 2–4, Tab. 3). The greatest increase was observed after the application of h.a. chernozem in relation to the control (treatment No. 1, Tab. 3). In the case of h.a. from Aldrich itself, dry matter of roots decreased, but at the same time they were elongated in relation to the control (treatment No. 1, Tab. 3). Natural humic preparations caused a decrease of common pea root length (treatments No. 3–4, Tab. 3).

In the presence of zinc and cadmium in the solution (treatments No. 5 and 9, Tab. 3), dramatic decrease of fresh and dry matter of aboveground parts as well as dry matter of roots and their shortening was recorded. After the amendment of zinc-containing treatments (No. 6–8) with humic preparations added to the me-

dium, slight quantitative changes of plant bio-mass and even a slight decrease of fresh matter (except h.a. from Aldrich), amounts of dry matter of aboveground parts (largest in the case of h.a. chernozem) and further root shortening were recorded. No changes of root dry matter in discussed "humic-zinc" treatments were observed. Analysis of "cadmium-humic" treatments (No. 10–12, Tab. 3) showed obvious quantitative increase of common pea bio-mass, both of above-ground parts and roots, as well as root elongation. However, the greatest changes took place in the treatment where humic acids by Aldrich company were added to Cd ions (treatment No. 10, Tab. 3).

No.	Treatment	Fresh mass g	Dry mass g	Dry mass of roots g	Average length of roots cm
1	0	14.56	3.10	2.47	41.80
2	0 + h.a. from Aldrich	15.28	3.40	2.11	44.75
3	0 + h.a. orthic luvisol	16.67	4.05	2.48	38.98
4	0 + h.a. haplic phaeozem	25.29	5.65	2.69	38.58
5	0 + Zn	0.84	0.38	0.09	8.33
6	0 + Zn + h.a. from Aldrich	1.01	0.34	0.09	4.18
7	0 + Zn + h.a. orthic luvisol	0.86	0.34	0.10	3.43
8	0 + Zn + h.a. haplic phaeozem	0.62	0.24	0.08	3.33
9	0 + Cd	0.98	0.35	0.14	3.98
10	0 + Cd + h.a. from Aldrich	4.67	0.97	0.39	5.45
11	0 + Cd + h.a. orthic luvisol	1.52	0.50	0.16	4.03
12	0 + Cd + h.a. haplic phaeozem	1.46	0.49	0.16	4.63
	x	6.98	1.65	0.91	16.79
$LSD_{0.05}$		4.70	1.19	0.30	15.08

Table 3. Biomass of investigated plants

Many authors agree that the presence of organic matter in the environment causes changes of heavy metals toxicity [Spiak 1998, Gorlach and Gambuś 2000, Badora 2002]. Decreasing of crop yields is one of the symptoms of toxic action of heavy metals towards plants. However, the plants reaction to stress is a complex phenomenon and difficult to systematize due to the character and properties of the elements and plants subjected to the exposure [Leavy *et al.* 1999, Cobbet 2000, Foulkes 2000, Williams *et al.* 2000]. The present study revealed that humic compound origin determines the amount of plant bio-mass produced under stress conditions because (i) the tested preparations were characterized with different properties, such as exchangeable capacity or number of functional groups, (ii) they de-toxicated zinc and cadmium ions in probably different manner, and (iii) the ratio of humic compounds to free zinc ions was too low.

The uptake of cadmium and zinc ions by tested plants is presented in Table 4. Presence of humic preparations alone in the treatments (No. 2–4, Tab. 4) clearly indicates diminished uptake of zinc ions from the medium at the presence of h.a. from Aldrich in relation to the control (treatment No. 1, Tab. 4) and as compared

to the other two humic preparations of natural origin. In treatments where free zinc ions occurred along with the applied preparations (treatments No. 6–8, Tab. 4), increase was recorded in zinc uptake by common pea roots in relation to treatment No. 5 where only free zinc ions were present. However, Zn^{2+} uptake was the lowest at the presence of h.a. from Aldrich. An obvious decrease was observed in zinc accumulation in aboveground parts of tested plants due to natural and artificial humic acids, while the best effects were achieved in treatments No. 6 (h.a. from Aldrich) and No. 8 (h.a. chernozem) (Tab. 4). Elevated cadmium ions uptake by roots of tested plants at the presence of h.a. from Aldrich (treatment No. 10, Tab. 4) in relation to treatment No. 9 (O + Cd) took place. The other humic preparations clearly decreased Cd^{2+} uptake by the plants roots (treatments No. 11–12, Tab. 4). All applied preparations reduced cadmium ion concentration in above ground parts of common pea (Tab. 4).

No	Treatment	0	Cd	Zn		
INO.	Treatment	roots	leaves	roots	leaves	
1	0	0.33	0.00	28.06	8.95	
2	0 + h.a. from Aldrich	0.42	0.23	16.77	9.38	
3	0 + h.a. orthic luvisol	0.31	0.00	29.83	11.26	
4	0 + h.a. haplic phaeozem	0.18	0.00	20.98	12.13	
5	0 + Zn	0.55	0.09	147.28	322.64	
6	0 + Zn + h.a. from Aldrich	0.19	0.06	155.51	243.15	
7	0 + Zn + h.a. orthic luvisol	0.28	0.03	192.23	295.68	
8	0 + Zn + h.a. haplic phaeozem	0.21	0.10	181.62	241.24	
9	0 + Cd	31.53	9.69	8.00	5.47	
10	0 + Cd + h.a. from Aldrich	36.78	7.20	5.78	6.24	
11	0 + Cd + h.a. orthic luvisol	13.16	7.32	5.33	3.33	
12	0 + Cd + h.a. haplic phaeozem	10.73	9.15	6.88	2.20	

Table 4. Uptake of zinc and cadmium by investigated plants (µg/plant)

Competition between Zn^{2+} and Cd^{2+} ions, having influence on both ions uptake by common pea, was observed as well. In the case of zinc excess in the solution, elevated uptake of cadmium ions occurred (treatment No. 5) as compared to treatment No. 1 (Tab. 4). The presence of cadmium ions in treatments where they were not added (treatments No. 1–8) might have resulted from impurities accompanying the minerals used as medium or from water contamination with compounds of the metal. Addition of free Cd^{2+} ions to treatments No. 9–12 (Tab. 4) diminished zinc ion uptake from the medium: the more, the larger the amount of humic preparations.

Naidu and Harter [1998] and Prasad and Hagemeyer [1999] found an influence of low-molecular organic acids excreted, among other by plant roots, on heavy metals complexing by solid soil components. Low-molecular organic acids used in the present experiments might have taken part in binding of the metal and solids (humic preparations) as mediate components. This could be another mechanism explaining the different effect of natural and artificial humic preparations towards the reduction of zinc and cadmium toxicity with relation to the tested plants.

CONCLUSIONS

- Varied influence of natural and artificial humic acids on binding of free zinc and cadmium ions in medium was observed, which might have resulted from (i) different sorption capacity and multi-functionality of tested preparations, (ii) different chemical properties of Cd²⁺ and Zn²⁺ ions, and (iii) varied ratios of preparation : metal ion.
- 2. Natural humic acids (h.a. lessive and h.a. chernozem) bonded zinc ions through COOH and OH moieties. Low reactivity of OH groups for Cd²⁺ ions and only partial binding by COOH groups was observed, but without clear preference of the type of natural preparation.
- 3. Humic acids from Aldrich company showed very great affinity both to zinc and cadmium ions, but binding with zinc was probably of specific and that with cadmium of non-specific character.
- 4. Amount of plant bio-mass and root length of tested common pea was significantly increased in "cadmium-zinc" treatments as compared to the 0 + Cd treatment, but the greatest changes were recorded following the application of the preparation produced by the Aldrich company. The two natural humic acids acted in similar way.
- 5. The lowest zinc ion uptake by pea roots under stress conditions was observed in the presence of h.a. from Aldrich. The h.a. chernozem preparation mostly reduced cadmium ion uptake by tested plants.

REFERENCES

- Alloway B.J., 1990. Heavy Metals in Soils. Blackie, Glasgow and London. John Wiley & Sons, Inc., New York.
- Badora A., 2002. Bioaccumulation of Al, Mn, Zn and Cd in pea plants (*Pisum sativum* L.) against the background of unconventional binding agents. Pol. J. of Environ. Stud. 11, 2, 109–116.
- Basta N.T., Gradwohl R., Snethen K.L., Shroder J.L., 2001. Chemical immobilization of lead, zinc and cadmium in smelter-contaminated soils using biosolids and rock phosphate. J. Environ. Qual. 30, 1222–1230.
- Bradshaw A., 2000. The use of natural processes in reclamation advantages and difficulties. Landscape and Urban Planning 51, 89–100.
- Brauner I., Bukatsch F., 1987. Practice of plants physiology (in Polish). PWN, Warszawa.
- Cobbet C.S., 2000. Phytochelatins and their roles in heavy metal detoxification. Plant Physiol. 123, 825–833.
- Evangelou P.V., Marsi M., Vandiviere M.M., 1999. Solubility of Ca²⁺, Cd²⁺, Cu²⁺ (illite-humic) complexes and pH influence. Plant and Soil 213, 63–74.
- Foulkes E.C., 2000. Transport of toxic metal across cell membranes. Proc. Soc. Exp. Biol. Med. 223, 234–240.
- Gambuś F., Rak M., 2000. Influence of soil properties on the solubility of cadmium compounds. Zesz. Probl. Post. Nauk Rol., 472, 251–257

- Gorlach E., Gambuś F., 2000. Potentially harmful trace elements in soils (redundancy, harmfuleness, opposition). Zesz. Probl. Post. Nauk Rol., 472, 275–296.
- Gunnela M. Gustafson, Eva Salomon, Simon Jonsson, 2007. Barn balance calculations of Ca, Cu, K, Mg, Mn, N, P, S and Zn in a conventional and organic dairy farm in Sweden. Agriculture, Ecosystems and Environment, 119, 160–170.
- Kononowa M., 1968. Soil Organic Matter (in Polish). PWN, Warszawa.
- Leavy B.D., Redente F.E., Uphoff D.G., 1999. Evaluating the phytotoxicity of Pb-Zn Tailings to big bluestern (*Antropogen Gerardii Vitamin*) and Switchgrass (*Panicum Virgatum* L.). Soil Sci., 164(6), 363–375.
- MacBride B.M., Martinez E.C., Topp E., Evans L., 2000. Trace metal solubility and Speciation in a calcareous soil 18 years after no-till sludge. App. Soil Sci., 165(8), 646–656.
- Naidu R., Harter D.R., 1998. Effect of different organic ligands on cadmium sorption by and exctractability from soils. Soil Sci. Soc. Am. J., 62, 644–650.
- Ostrowska A., Gawlińska S., Szczubiałka K., 1991. Estimation of methods of plants and soils properties. Catalog, Warszawa, 225–226.
- Prasad M.N.V., Hagemeyer J., 1999. Heavy metal stress in plants (from molecules to ecosystems). Springer-Verlag, Berlin, Heilderberg, 1.
- Rogóż A., 2002. Content and imbibition of trace elements by plants during variable soils reaction.P. I. Content and imbibition of Cu, Zn oraz Mn by plants. P. II. Content and imbibition of Cd, Ni i Pb by plants. Zesz. Probl. Post. Nauk Rol., 482, 439–451.
- Shuman M.L., 1999. Effect of organic waste amendments on zinc adsorption by two soils. Soil Sci. 164(3), 197–205.
- Sosulski T., Łabętowicz J., Janczyk M., Szymańska M., 2007. The influence of industrial wastesgypsum and phosphogypsum on the content of Zn, Cd, and Pb in plants and soil. Zesz. Probl. Post. Nauk Rol., 520, 379–388.
- Sparks D.L., 1995. Environmental Soil Chemistry. San Diego, New York, Boston, London, Sydney, Tokyo, Toronto, Academic Press, 1–320.
- Spiak Z., 1998. The influence of soil reaction on the imbibition of Zn by plants. Zesz. Probl. Post. Nauk Rol. 456, 439–443.
- Spiak Z., Romanowska M., Radoła J., 2000. The trace content of Zn in soils for various plants. Zesz. Probl. Post. Nauk Rol., 471, 1125–1134.
- Sposito G. (ed.), 1989. The Environmental Chemistry of Aluminium. Boca Raton, CRC Press, p. 317.
- Stevenson F.J., 1994. Humus Chemistry. Genesis, Composition, Reactions. (sec. ed.), New York, Chichster, Brisbane, Toronto, Singapore. John Wiley & Sons, 1–530.
- Usman A.R.A., Kuyakov Y., Lorenz K., Stahr K., 2006. Remediation of a soil contaminated with heavy metals by immobilizing compounds. J. Plant Nutr. Soil Sci., 169, 205–212.
- Williams L.E., Pittman J.K., 2000. Emerging mechanisms for heavy metal transport in plants. Biochim. et Biophys. Acta 1465, 104–126.

Wpływ naturalnych i sztucznych kwasów huminowych na ograniczanie toksyczności Zn i Cd dla roślin grochu siewnego (*Pisum sativum* L.)

WPŁYW NATURALNYCH I SZTUCZNYCH KWASÓW HUMINOWYCH NA OGRANICZANIE TOKSYCZNOŚCI Zn I Cd DLA ROŚLIN GROCHU SIEWNEGO (Pisum sativum L.)

Streszczenie. Celem niniejszych badań było określenie wpływu sztucznych i naturalnych kwasów huminowych na zmiany toksyczności jonów kadmu i cynku dla roślin grochu zwyczajnego (*Pisum sativum* L.). W badaniach stwierdzono zróżnicowany wpływ naturalnych i sztucznych kwasów huminowych na wiązanie wolnych jonów cynku i kadmu w pożywce, co mogło wynikać z: (i) odmiennej pojemności sorpcyjnej i polifunkcyjności badanych preparatów; (ii) z odmiennych właści-wości chemicznych jonów Cd²⁺ i Zn²⁺; (iii) z odmiennego stosunku: preparat : jon metalu. Naturalne kwasy huminowe (h.a. płowa i h.a czarnoziem wiązały jony cynku poprzez grupy COOH i OH. Natomiast kwasy huminowe firmy Aldrich wykazywały bardzo duże powinowactwo zarówno do jonów cynku, jak i do jonów kadmu, przy czym wiązanie z cynkiem miało prawdopodobnie charakter specyficzny, a z kadmem niespecyficzny. Najmniejsze pobranie jonów cynku przez korzenie roślin grochu w warunkach stresowych odnotowano w obecności h.a. z firmy Aldrich, natomiast preparat h.a. czarnoziem w największym stopniu ograniczał pobieranie jonów kadmu przez badane rośliny.

Słowa kluczowe: naturalne i sztuczne kwasy huminowe, toksyczność cynku i kadmu, groch siewny