FOLIA
HORTICULTURAE
Ann. 19/1, 2007, 87-96

The effect of nitrogen fertilizer form and foliar application on Cd, Cu and Zn concentrations in carrot

Sylwester Smoleń, Włodzimierz Sady

Department of Soil Cultivation and Fertilization of Horticultural Plants
Faculty of Horticulture, Agricultural University in Kraków
29 Listopada 54, 31-425 Kraków, Poland
e-mail: ssmolen@bratek.ogr.ar.krakow.pl

Key words: carrot, nitrogen fertilization, cadmium, copper, zinc, biological quality of vegetable

ABSTRACT

Two sub-blocks were distinguished in a pot experiment with carrot 'Kazan F_1' cultivation: with and without plant foliar application. The plants were treated thrice with foliarly applied 2% urea solution, 1% solution of 'Supervit R' multi-component fertilizer and again with 2% urea solution. Nitrogen fertilization used within the sub-blocks included: the control (unfertilized with nitrogen), $Ca(NO_3)_2$, NH_4NO_3, $(NH_4)_2SO_4$ and $CO(NH_2)_2$. The roots of plants fertilized with $(NH_4)_2SO_4$ contained the largest quantities of Cd and Zn. The forms of fertilizer (N) did not affect carrot Cu concentrations. Foliar application raised Cu contents but had no statistically significant effect on Cd or Zn concentrations in carrot.

INTRODUCTION

The effect of fertilization (including mineral nitrogen treatment) on the level of heavy metal accumulation in yield depends on many factors. These are, among the others, connected with physico-chemical properties of soil, particularly with soil type, texture, redox potential, organic substance content (Gębski 1998, Kabata-Pendias and Pendias 1999, Sady and Smoleń 2004), total cation exchange capacity, base saturation ratio, Ca and Mg content in soil but also total contents of heavy metals (Gambuś 1993, Sady and Rożek 2002).

Diatta and Grzebisz (2006) demonstrated that the effect of both fertilizer (N) forms (NH_4NO_3, $CO(NH_2)_2$, $NH_4NO_3 \cdot CaCO_3$) and nitrogen dose (100 and 200 kg N ha^{-1}) on Cd, Cu, Pb and Zn concentrations in soil was associated with buffer properties of soil. The research conducted by Gębski and Mercik (1997) on red beetroots and lettuce cultivation in the soil naturally polluted and artificially enriched with Cd, Pb and Zn revealed significantly higher concentrations of these elements in plants fertilized with $(NH_4)_2SO_4$ and NH_4NO_3 than in those treated with $NaNO_3$. In the studies conducted by Rodríguez-Ortíz et al. (2006) NH_4NO_3 treatment dosed 50, 100 and 150 mg N kg^{-1} of soil increased Cd and Pb accumulation in tobacco to greater extent than fertilization with $CO(NH_2)_2$ dosed 50 and 100 mg N kg^{-1} of soil.

Considering the level of heavy metal accumulation in yield, the effect of foliar application and its interaction with nitrogen fertilization have not been sufficiently diagnosed.

The research aimed at assessing $Ca(NO_3)_2$, NH_4NO_3, $(NH_4)_2SO_4$ and $CO(NH_2)_2$ and foliar nutrition effect on Cd, Cu and Zn content in carrot.

MATERIAL AND METHODS

In 2004 – 2005 'Kazan F_1' carrot was cultivated in latticed containers 60 × 40 × 20 cm, placed in the open field under a shadow fabric. The containers were filled with medium silt loam (3% sand, 28% silt and 37% clay) with the mean content of organic substance of 3.25%, and the following concentrations of element forms soluble in 0.03M acetic acid: N ($N\text{-}NO_3$+$N\text{-}NH_4$) 28.0 mg, P 4.3 mg, K 28.8 mg, Mg 137.4 mg and Ca 1424.7 mg in 1 dm^3 of soil, and average total contents of Cd 1.04 mg, Cu 45.0 mg and Zn 202.1 mg per 1 kg of soil. The total sorption capacity of the soil used for the experiment was 11.2 $cmol^{(+)}$ kg^{-1} at 89.8% base saturation ratio. The soil reaction pH_{H_2O} was 7.29, pH_{KCl} 6.70 while total salt concentration was on the level of 0.45 EC in mS cm^{-1}.

Seeds were sown on 20.04.2004 and on 27.04.2005. The content of assimilable nutrient forms during vegetation period was maintained on the following levels: P

80 mg, K 120 mg, Mg 80 mg, Ca 2000 mg dm^{-3} of soil by means of fertilization (based on the results of soil chemical analysis) conducted on 8.04. and 5.07. in 2004 and on 25.04. and 1.07. in 2005. Nutrients were supplied to the soil as fertilizers: KH_2PO_4, K_2SO_4 (as soluble fertilizer produced by Yara), $MgSO_4 \cdot 7\ H_2O$ with microelements (comprising: 0.35% Mn, 0.3% Cu, 0.2% Zn, 0.05% B and 0.01% Mo, produced by Intermag) and $CaCO_3$ (produced by EKO-WAP). With the fertilizer $MgSO_4 \cdot 7\ H_2O$ were supplied to soil with microelements ca. 2.5 mg Cu and 1.66 mg Zn dm^{-3} soil. The soil was fertilized with nitrogen thrice during the vegetation period (i.e. on 20.04., 5.07. and 23.08.2004, and on 25.04., 1.07. and 22.08.2005) based on the results of soil chemical analysis, in order to supplement the N-mineral content to the level of 100 mg N dm^{-3} of soil.

The research comprised two sub-blocks with plant foliar application and without foliar nutrition. In the sub-block with foliar application the plants were sprayed thrice (on 30.06., 6.08. and 24.08. in 2004 and 28.06., 1.08. and 23.08. in 2005) with 2% of urea solution, 1% of Supervit R fertilizer solution and again with 2% urea solution. 'Supervit R' fertilizer contains (percentage by weight): 3.5% N (1.0% N-NO_3, 2.5% N-NH_2), 3.4% K_2O, 0.6% MgO, 0.04% Mn and 0.02% B, Cu, Ti and Zn – each, 0.012% Fe and 0.001% Mo. The following objects with soil fertilized with nitrogen were distinguished within the sub-blocks: 1 – control (unfertilized with nitrogen), 2 – $Ca(NO_3)_2$, 3 – NH_4NO_3, 4 – $(NH_4)_2SO_4$ and 5 – $CO(NH_2)_2$. Nitrogen was supplied to the soil as fertilizer produced by: $Ca(NO_3)_2$ (as soluble fertilizer) – Yara, NH_4NO_3, $CO(NH_2)_2$ – Zakłady Azotowe in Puławy, $(NH_4)_2SO_4$ – Zakłady Azotowe in Tarnów.

Carrot was harvested and its yield was assessed on 15.09.2004 and 27.09.2005. At the same time the soil was sampled for analyses from the sub-block where foliar application was not applied. The soil reaction pH_{H_2O} was assessed by potentiometer (Nowosielski 1988) and organic matter with Tiurin method modified by Oleksynowa (Komornicki et al. 1991). Base saturation ratio was determined with AAS method after soil extraction with 1M NH_4Cl (Kociałkowski et al. 1984). Total content of Cd, Cu and Zn content in soil were assessed using *Aqua Regia* method (Houba et al. 1997b), readily soluble forms of Cd, Cu and Zn in soil were assessed after extraction with 0.01M $CaCl_2$ (Houba et al. 1997a). Cd, Cu and Zn concentrations in carrot roots were determined after mineralization of fresh plant material in a mixture of $HNO_3 : HClO_4 : H_2SO_4$ in the 6 : 2 : 0.25 ratio (Jędrzejczak 1991). The assessments of Cd, Cu and Zn in the soil and plant material samples were conducted with AAS method. Statistical computations of the obtained results were conducted using ANOVA module of Statistica 6.1 programme for $p = 0.05$.

RESULTS

As shown by the results included in Table 1, nitrogen applied for fertilization in the form of NH_4NO_3, $(NH_4)_2SO_4$ and $CO(NH_2)_2$ caused a distinctive decline in soil reaction pH_{H_2O} in comparison with the control and the $Ca(NO_3)_2$ treatment. Apparent differences were also noted in the soil Cu concentrations in effect of applied nitrogen fertilizer forms. The content of easily assimilable forms of this component evidently decreased in comparison with the control after $Ca(NO_3)_2$ treatment but increased in result of NH_4NO_3 and $CO(NH_2)_2$ treatments. No statistically significant differences were demonstrated for the concentrations of readily soluble Cd and Zn forms in soil depending on the analyzed objects. However, an obvious tendency for the content of easily assimilable forms of Cd and Zn to increase after $(NH_4)_2SO_4$ and $CO(NH_2)_2$ fertilization should be noticed, as well a tendency for Zn concentrations to grow following NH_4NO_3 fertilization, as compared with the control.

Table 1. Soil reaction and the contents of readily soluble forms of cadmium, copper and zinc (assessed in 0.01M $CaCl_2$) in soil after carrot cultivation – means for 2004 – 2005

N-form for fertilization	pH_{H_2O}	(mg kg^{-1} soil)		
		Cd	Cu	Zn
Control	6.77	0.56	4.60	44.68
$Ca(NO_3)_2$	6.73	0.59	3.71	45.01
NH_4NO_3	6.41	0.56	5.20	48.59
$(NH_4)_2SO_4$	6.07	0.64	4.86	49.64
$CO(NH_2)_2$	6.51	0.67	5.31	47.58
LSD (for fertilization)	0.087	n.s.	0.324	n.s.

The results of soil chemical analysis revealed statistically significant raise of Cd content in storage roots of the carrot fertilized with nitrogen as compared with the control, unfertilized with this component. The largest quantities of Cd were found in the carrot fertilized with $(NH_4)_2SO_4$ (Table 2). However, no statistically significant effect of foliar application on Cd concentrations in carrot was demonstrated although a slight increase of this element content in the plants receiving foliar application and nitrogen fertilization as $(NH_4)_2SO_4$ and $CO(NH_2)_2$ should be noticed (Fig. 1). Nitrogen fertilization also caused a statistical growth in Zn content in the carrot following the application of NH_4NO_3, $(NH_4)_2SO_4$ and $CO(NH_2)_2$, whereas foliar application had no apparent effect on the concentrations of this element in plants (Table 2, Fig. 3). No statistically significant differences were demonstrated for carrot Cu concentrations in effect of nitrogen fertilizers applied to the soil (Table 2). On the other hand, in carrot receiving foliar feeding, a markedly higher copper content was recorded than in the plants without this treatment (Table 2). The highest Cu concentrations were found in the plants fertilized with $(NH_4)_2SO_4$ for which also foliar application was applied (Fig. 2).

Table 2. Cadmium, copper and zinc concentrations in carrot storage roots depending on fertilization and foliar application – means for 2004 – 2005

N-form for fertilization	(mg kg^{-1} f.w.)		
	Cd	Cu	Zn
Control	0.046	0.732	3.963
$Ca(NO_3)_2$	0.068	0.654	4.442
NH_4NO_3	0.065	0.623	4.867
$(NH_4)_2SO_4$	0.100	0.985	6.387
$CO(NH_2)_2$	0.068	0.908	5.381
LSD (for fertilization)	0.0158	n.s.	0.5309
Mean for foliar application	Cd	Cu	Zn
Without foliar application	0.067	0.461	4.862
With foliar application	0.072	1.100	5.154
LSD (for foliar application)	n.s.	0.3786	n.s.

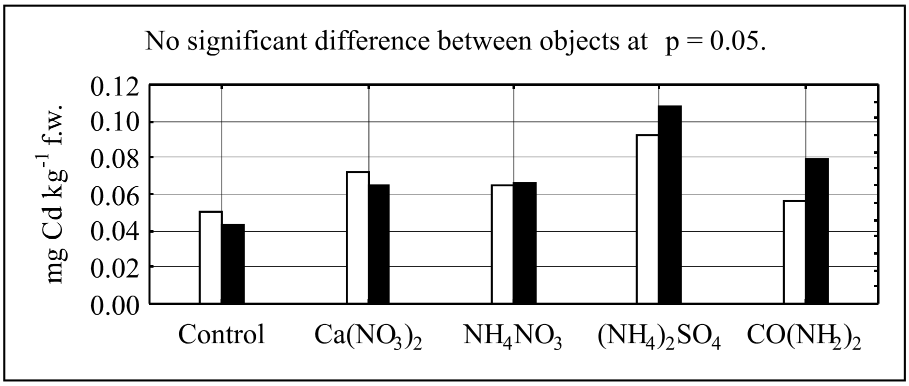

Fig. 1. Content of cadmium in carrot storage roots concerning soil fertilization and foliar feeding; □ without foliar nutrition, ■ with foliar nutrition

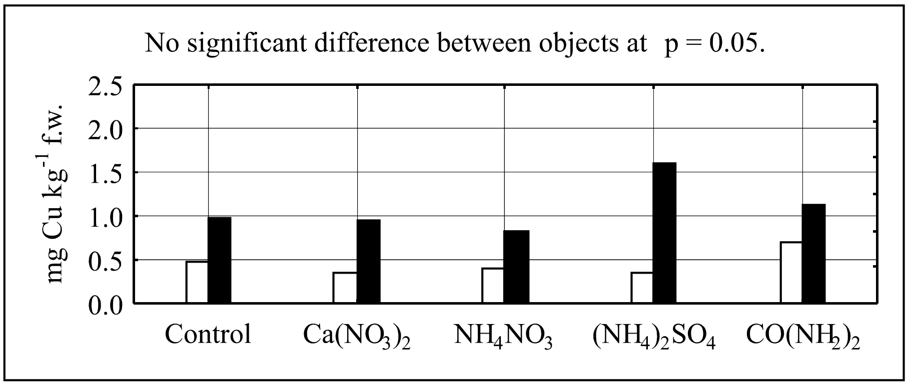

Fig. 2. Content of copper in carrot storage roots concerning soil fertilization and foliar feeding; □ without foliar nutrition, ■ with foliar nutrition

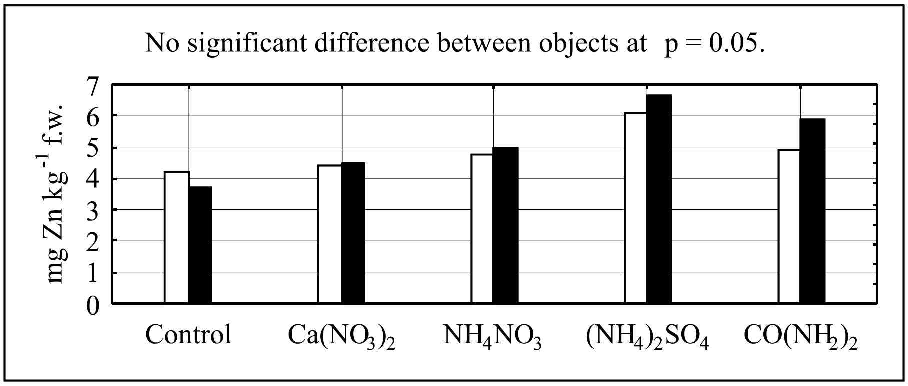

Fig. 3. Content of zinc in carrot storage roots concerning soil fertilization and foliar feeding; □ without foliar nutrition, ■ with foliar nutrition

DISCUSSION

Physiologically acid nitrogen fertilizers, such as $(NH_4)_2SO_4$, NH_4NO_3 and $CO(NH_2)_2$, caused the lowering of the reaction of soil (in comparison to the control and fertilization $Ca(NO_3)_2$) however the results of analyses demonstrate that the application of these fertilizers relatively affected the content of readily soluble forms of Cd, Cu and Zn in soil. The obtained results have been somehow corroborated by the research conducted by Czekała and Jakubus (2006) and Łukowski (2006). The studies of Czekała and Jakubus (2006) revealed that nitrogen fertilization dosed 0, 68.2, 125.7 and 188.6 kg N ha^{-1} (applied for several different crop rotations) had slight effect on the content of soluble forms of Cu, Mn and Ni but not Zn in soil. The highest content of Zn was registered in the top soil layer (0-30 cm) after the application of higher nitrogen doses. Łukowski (2006) revealed that nitrogen fertilization (with urea, multi component fertilizers, phosphorus and phosphorus-potassium fertilizers) did not have any influence on the content of mobile Zn forms in soil in the first and second year after the treatment.

Despite a relatively slight effect of the nitrogen fertilizers used in the experiment upon the content of readily soluble forms of Cd, Cu and Zn in soil, $(NH_4)_2SO_4$ treatment a raise in Cd, Zn and Cu content in carrot storage roots influenced the most. The obtained results confirm the findings of the other authors (Jurkowska and Rogóż 1981, Gębski and Mercik 1997, Gębski 1998, Sady and Smoleń 2004) emphasizing the fact that $(NH_4)_2SO_4$ fertilization to the greatest extent affects the increase of heavy metal accumulation in yield in comparison with the other nitrogen fertilizers. Hassan et al. (2005) revealed that the effect of fertilizer nitrogen (N) form on Cd accumulation level in plants is associated with the concentrations of biovailable forms of this element in the rhizosphere. However, these authors in their experiments on rice cultivation on the medium containing 1 μM Cd, registered a higher level of Cd accumulation in roots and shoots at fertilization with $Ca(NO_3)_2$ and NH_4NO_3 than at $(NH_4)_2SO_4$ treatment.

In the presented experiment nitrogen content in soil was maintained on the optimal level for plant nutritional needs (thrice nitrogen fertilization during cultivation) for the whole period of cultivation. It might have to some extent, strengthened both the physico-chemical effect of nitrogen fertilizers upon the soil environment (potential seasonal changes of bioavailable forms of heavy metals in soil) and physiological plant response to the soil environment. It may have contributed to the increased Cd and Zn content in carrot in comparison with the control that was unfertilized with nitrogen. However, the results of pot experiments are not always corroborated by these obtained in a field cultivation. Former experiments (Smoleń and Sady 2006) on carrot field cultivation revealed that $Ca(NO_3)_2$ and NH_4NO_3 fertilization (dosed 70 and 70+70 kg N ha^{-1}) had no effect on Cd, Cu and Zn concentrations in storage roots.

In the investigations mentioned above (Smoleń and Sady 2006), foliar application (according to the design analogous as in the presented work) caused a significant increase in Cd accumulation level but a decline in Cu, whereas it did not affect Zn content in carrot. On the other hand, in the discussed research results, an almost 138% increase in Cu concentration was registered, as well as elevated contents of Cd and Zn in carrot (despite no statistical differences) under the influence of foliar application. The obtained results are quite difficult to interpret. Foliar application might have produced a specific plant reaction leading to the increase of the quantities of these elements in carrot. Adamec (2002) demonstrated that foliar application may stimulate uptake of some minerals by roots, which contributes to their accumulation in plants. On the other hand a mechanism of nutrient (which are cations) uptake by roots causes H^+ release into the rhisoshpere. Hydrogen protons cause a decrease in soil reaction, which results in the increased content of bioavailable forms of heavy metals in the substratum. According to Yang et al. (2005), H^+ release by root system is one of the reasons for accelerating the rate of microbiological mobilization of heavy metals in the rhizosphere and therefore increasing their accumulation in plants.

CONCLUSIONS

1. Applied forms of fertilizer (N) affected a decrease in the soil reaction (pH). $CO(NH_2)_2$ and NH_4NO_3 fertilization increased, whereas $Ca(NO_3)_2$ decreased, the content of readily soluble Cu forms in soil. Fertilizer (N) forms had no influence upon Cd and Zn concentrations in soil after carrot cultivation.
2. Carrot storage roots fertilized with $(NH_4)_2SO_4$ contained the highest amounts of Cd and Zn in comparison with the control plants or those fertilized with different nitrogen fertilizers. Fertilizer (N) forms had no effect on Cu concentrations in carrot.
3. Foliar application raised Cu content but had no influence on Cd and Zn concentrations in carrot storage roots.
4. No statistically significant interaction between foliar application and fertilization on Cd, Cu or Zn concentrations in carrot was found.

REFERENCES

ADAMEC L., 2002 (abs.). Leaf absorption of mineral nutrients in carnivorous plants stimulates root nutrient uptake. New Phytol. 155(1): 89.

CZEKAŁA J., JAKUBUS M., 2006. Influence of long-term plant cultivation and nitrogen fertilization on the content of soluble forms of trace elements in a lessive soil. Pol. J. Environ. Stud. 15 (2a), Part I: 36-41.

DIATTA J.B., GRZEBISZ W., 2006. Influence of mineral nitrogen forms on heavy metals mobility in two soils. Pol. J. Environ. Stud. 15 (2a), Part I: 56-62.

GAMBUŚ F., 1993. Metale ciężkie w wierzchniej warstwie gleb i w roślinach regionu krakowskiego. Zesz. Nauk. AR w Krakowie. Rozp. Habil. 176. [In Polish]

GĘBSKI M., 1998. Czynniki glebowe oraz nawozowe wpływające na przyswajanie metali ciężkich przez rośliny. Post. Nauk Roln. 5: 3-16. [In Polish with English summary]

GĘBSKI M., MERCIK S., 1997. Effectivenes of fertiliser from in acumulation of zinc, cadmium and lead in lettuce (*Lactuca sativa* L.) and Red beet (*Beta vulgaris* var. *cicla* L.). Ecological aspects of nutrition and alternatives for herbicides in horticulture – Int. Sem. Warsaw: 23-25.

HASSAN M.J., WANG F., ALI S., ZHANG G., 2005. Toxic effect of cadmium on rice as affected by nitrogen fertilizer form. Plant Soil 277: 359-365.

HOUBA V.J.G., VAN DER LEE J.J., NOVOZAMSKY I., 1997a. Soil analysis procedures, Other Procedures (Soil and Plant analysis, part 5B). Wageningen Agricultural University, The Netherlands, 262 pp.

HOUBA V.J.G., NOVOZAMSKY I., TEMMINGHOFF E., 1997b. Soil analysis procedures. Extraction with 0.01 M $CaCl_2$ (Soil and Plant Analysis, Part 5A). Wageningen Agricultural University, The Netherlands, 93 pp.

JĘDRZEJCZAK R., 1991. Determination of the content of arsenic, lead, copper, zinc and tin in bottled fruit, fruit pulp and jams by the method atomic absorption spectrophotometry /AAS/. Prace Inst. i Lab. Bad. Przem. Spoż. 43: 31-41. [In Polish with English summary]

JURKOWSKA H., ROGÓŻ A., 1981. Wpływ formy i dawki azotu na zawartość makro i mikroelementów w roślinach. Część II: Mikroelementy. Acta Agr. Silv. Ser. Agr. 20: 121-131. [In Polish with English summary]

KABATA-PENDIAS A., PENDIAS H., 1999. Biogeochemia pierwiastków śladowych. Wyd. II. PWN, Warszawa, 398 pp. [In Polish]

KOCIAŁKOWSKI W.Z., POKOJSKA U., SAPEK B., 1984. Przewodnik metodyczny do oznaczania pojemności sorpcyjnej gleb. Prace Komisji Naukowych PTG. II 14, Warszawa, 94 pp. [In Polish]

KOMORNICKI T., OLEKSYNOWA K., TOKAJ J., JAKUBIEC J., 1991. Przewodnik do ćwiczeń z gleboznawstwa i geologii. Cz. II. Metody laboratoryjne analizy gleb. Skrypt AR w Krakowie, 140 pp. [In Polish]

ŁUKOWSKI A., 2006. The influence of mineral fertilization on heavy metal fraction contents in soil. Part I. Pol. J. Environ. Stud. 15(2a), Part II: 410-414.

NOWOSIELSKI O., 1988. Zasady opracowywania zaleceń nawozowych w ogrodnictwie. PWRiL, Warszawa, 312 pp. [In Polish]

RODRÍGUEZ-ORTÍZ J.C., VALDEZ-CEPEDA R.D., LARA-MIRELES J.L., RODRÍGUEZ-FUENTES H., VÁZQUEZ-ALVARADO R. E., MAGALLANES-QUINTANAR R., GARCÍA-HERNÁNDEZ J.L., 2006. Soil nitrogen fertilization effects on phytoextraction of cadmium and lead by tobacco (*Nicotiana tabacum* L.). Biorem. J. 10(3): 105-114.

SADY W., ROŻEK S., 2002. The effect of physical and chemical soil properties on the accumulation of cadmium in carrot. Acta Hort. 571: 73-75.

SADY W., SMOLEŃ S., 2004. Wpływ czynników glebowo-nawozowych na akumulację metali ciężkich w roślinach. Rocz. AR w Poznaniu, XXXCLVI, Ogrodn. 37: 269-277. [In Polish]

SMOLEŃ S., SADY W., 2006. The content of Cd, Cu and Zn in carrot storage roots as related to differentiated nitrogen fertilization and foliar nutrition. Polish J. Environ. Stud. 15 (2a), Part II: 503-509.

YANG X., FENG Y., HE Z., STOFFELLA P.J., 2005. Molecular mechanisms of heavy metal hyperaccumulation and Phytoremediation. J. Trace Elem. Med. Biol. 18: 339-353.

WPŁYW FORMY AZOTU I DOKARMIANIA DOLISTNEGO NA ZAWARTOŚĆ CD, CU I ZN W MARCHWI

Streszczenie: W latach 2004 – 2005 przeprowadzono doświadczenie wazonowe z uprawą marchwi 'Kazan F_1'. Marchew uprawiano w pojemnikach ażurowych o wymiarach 60 × 40 × 20 cm, umieszczonych na terenie otwartym pod cieniówką. Badaniami objęto dwa podbloki z dolistnym i bez dolistnego dokarmiania roślin. Rośliny dokarmiano dolistnie trzykrotnie: 2% roztworem mocznika, 1% roztworem nawozu wieloskładnikowego Supervit R i ponownie 2% roztworem mocznika. W obrębie podbloków zastosowano doglebowe nawożenie azotem: kontrola (nienawożona azotem), $Ca(NO_3)_2$, NH_4NO_3, $(NH_4)_2SO_4$, i $CO(NH_2)_2$. Najwięcej Cd i Zn zawierały korzenie spichrzowe roślin nawożonych $(NH_4)_2SO_4$. Formy azotu nie wpłynęły na zawartość Cu w marchwi. Dokarmianie dolistne podwyższyło zawartości Cu, nie miało natomiast wpływu na koncentrację Cd i Zn w marchwi. Nie stwierdzono statystycznie istotnego współdziałania dokarmiania dolistnego z nawożeniem na zawartość Cd, Cu i Zn w marchwi.

Received January 18, 2007; accepted June 25, 2007