

Janina GOSPODAREK¹ and Aleksandra NADGÓRSKA-SOCHA²

**EFFECT OF LIMING OF HEAVY METAL POLLUTED SOIL
ON THE CONTENT OF MAGNESIUM, CALCIUM AND IRON
IN BROAD BEAN (*Vicia faba* L., ssp. *maior*) PLANTS**

**WPLYW WAPNOWANIA GLEBY SKAŻONEJ METALAMI CIĘŻKIMI
NA ZAWARTOŚĆ MAGNEZU, WAPNIA I ŻELAZA W ROŚLINACH BOBU
(*Vicia faba* L., ssp. *maior*)**

Abstract: The research aimed at determining the effect of diversified lime doses on the content of magnesium, calcium and iron in broad bean plants growing in conditions of soil polluted with heavy metals on the III level of pollution according to the IUNG classification. Analyses were conducted on broad beans (*Vicia faba* L. ssp. *maior*), White Windsor c.v. cultivated in two series: in limed and non-limed soil. In each series the plants were cultivated in the following objects: unpolluted soil with natural heavy metal concentrations (Control); unpolluted soil with natural heavy metal content receiving mineral fertilization (NPK); soil polluted with cadmium dosed 4 mg · kg⁻¹ d.m.; soil contaminated with lead dosed 530 mg · kg⁻¹ d.m.; soil contaminated with copper dosed 85 mg · kg⁻¹ d.m.; soil polluted with 1000 mg · kg⁻¹ d.m. of zinc and soil contaminated with a dose of 110 mg · kg⁻¹ d.m. of nickel. Liming was conducted on the basis of hydrolytic acidity analysis of soil from individual objects. Two doses were applied: according to 1 and 2 Hh. The lime doses were respectively: Control – 356 and 712 mg CaO · kg⁻¹ d.m.; NPK – 420 and 840 mg CaO · kg⁻¹ d.m.; cadmium polluted soil – 504 and 1008 mg CaO · kg⁻¹ d.m.; soil polluted with lead – 420 and 840 mg CaO · kg⁻¹ d.m.; copper contaminated soil – 398 and 796 mg CaO · kg⁻¹ d.m.; soil polluted with zinc – 860 and 1720 mg CaO · kg⁻¹ d.m. and soil polluted with nickel 524 and 1048 mg CaO · kg⁻¹ d.m.

Soil contamination with heavy metals such as Cu, Cd, Pb, Ni or Zn causes considerable changes in Ca, Mg and Fe concentrations in broad bean plants. Application of liming contributes to balancing the content of the studied elements in plants. After the measure was applied the content of Ca, Fe and Mg in the plants growing in soil contaminated with individual heavy metals in most cases was on a level similar as in the plants growing in unpolluted soil.

Keywords: heavy metals, liming, accumulation, Mg, Ca, Fe

The harmful effect of heavy metals in soil may be revealed as blocking the uptake of some macro- and microelements by plants. For instance, Zn and Cd have an inhibitory

1 Department of Agricultural Environment Protection, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31-120 Kraków, Poland, email: rrjgospo@cyf-kr.edu.pl

2 Department of Ecology, University of Silesia, ul Bankowa 9, 40-007 Katowice, Poland, email: olan@hoga.pl

effect upon Fe, whereas lead on P and Mn absorption. Disturbances in the uptake of these elements may result in their deficiency in plants but may also reduce the nutritional value of plants cultivated for forage. Calcium in soil is identified as an agent neutralising the negative effect of many harmful constituents, including heavy metals [1, 2].

The investigations aimed at determining the effect of diversified calcium doses on the content of selected elements: magnesium, calcium and iron in broad bean plants growing in conditions of soil contaminated with heavy metals on the III level of pollution according to the IUNG classification [3].

Material and methods

The soil used for the experiment was a degraded chernozem developed from loess with acid reaction (pH in 1 mol · dm⁻³ KCl solution was 5.7 and in water 6.5) and organic carbon content 1.13 %. The observations were conducted on broad bean (*Vicia faba* L. ssp. *maior*), White Windsor, c.v. cultivated in two series: in limed and non-limed soil. The doses of heavy metals and calcium are given in Table 1. The way in which heavy metals were supplied to the soil, the amount of basic fertilization and methods of chemical analyses conducted on the soil were presented in other papers [4, 5]. Liming was conducted on the basis of hydrolytic acidity analyses of the soil from individual objects. Two doses were applied: according to 1 (...+Ca1) and 2 Hh (...+Ca2). The soil reaction from individual objects after the end of the growing period was presented in another paper [6].

Table 1

Experimental design

Object	Metal dose [mg/kg soil d.m.]	CaO dose [mg/kg soil d.m.] (acc. to 1 Hh) (+Ca1)	CaO dose [mg/kg soil d.m.] (acc. to 2 Hh) (+Ca2)
Non-fertilized control	–	356	712
Control receiving mineral fertilizers	–	420	840
Cadmium contaminated soil	4	504	1008
Copper contaminated soil	85	398	796
Lead contaminated soil	530	420	840
Nickel contaminated soil	110	524	1048
Zinc contaminated soil	1000	860	1720

The samples for chemical analyses were collected at the stage of seed milk maturity. Chemical analysis of the plant material consisted in determining the content of selected macroelements: iron, magnesium and calcium.

Plant material was washed in tap and in distilled water, dried at 105 °C to a constant weight and ground to fine powder, then mineralized and dissolved in 10 % HNO₃. After filtration: Mg, Ca, Fe content was measured using Flame Atomic Absorption Spec-

trometry (FAAS) [7, 8]. The quality of the analytical procedure was controlled by using samples of the reference material in each series of analysis (Certified Reference material CTA-OTL-1 Oriental Tobacco Leaves). The data were processed using software Statistica to compute significant statistical differences between samples ($p < 0.05$) according to Tukey's multiple range test.

Results and discussion

Soil contamination with copper, nickel and zinc caused a significant decline in magnesium concentrations in broad bean shoots in comparison with the objects with unpolluted soil (Fig. 1A). The decline was slight for copper, in the case of nickel it was almost two-fold, whereas for zinc even 5-fold. Liming of copper contaminated soil (both using a higher and a lower dose) led to a further slight decrease in the Mg content. A similar result of liming was observed when broad bean was growing in cadmium contaminated soil. In conditions of nickel polluted soil a double lime dose diminished the magnesium content in broad bean shoots by 1/3 in comparison with the object contaminated with this metal but without liming. On the other hand in the case of zinc contaminated soil, liming (both at the lower and higher CaO dose) incurred growth in the Mg content reaching almost the level similar to unpolluted plants. However, liming did not affect the content of magnesium in the shoots of broad bean cultivated in lead contaminated soil. Due to soil pollution with cadmium or lead, between 3 and 4 times larger amounts of magnesium were detected in broad bean roots growing in this soil than in the control plant roots (Fig. 1B). In conditions of copper and cadmium contaminated soils, a double dose of lime significantly lowered magnesium concentrations in broad bean roots. In broad bean grown in lead contaminated soil, a high, over two fold decline in magnesium concentration in the roots was registered when liming was done with both the lower and the higher dose.

This measure made the Mg content in roots approximate the same level as in plants unpolluted with heavy metals. Liming of zinc polluted soil caused an increase in the Mg content in broad bean underground parts, particularly at a higher lime dose. In nickel contaminated soil a lower dose of lime slightly elevated the Mg content in these plant parts, whereas a higher dose did not lead to any notable changes in this macroelement content. Similarly, a slight increase in the magnesium content under the influence of liming was noted in broad bean roots growing in the soil contaminated with a joint dose of heavy metals on the level corresponding to the I pollution degree according to the IUNG classification [9].

Soil pollution with all of the analyzed heavy metals, except cadmium, led to a decline in the calcium content in broad bean shoots (Fig. 2A). Liming of copper polluted soil apparently did not affect the concentration of this element. In the case of soil pollution with cadmium liming with both a higher and a lower dose led to a decline in the Ca content in broad bean shoots by ca 1/3. When the soil was polluted with lead the lower dose of lime elevated the Ca content (almost twice in comparison with Pb contaminated but non-limed soil), whereas the higher dose lowered this concentration (by ca 1/3 in comparison with the non-limed object). In conditions of soils contaminated with zinc

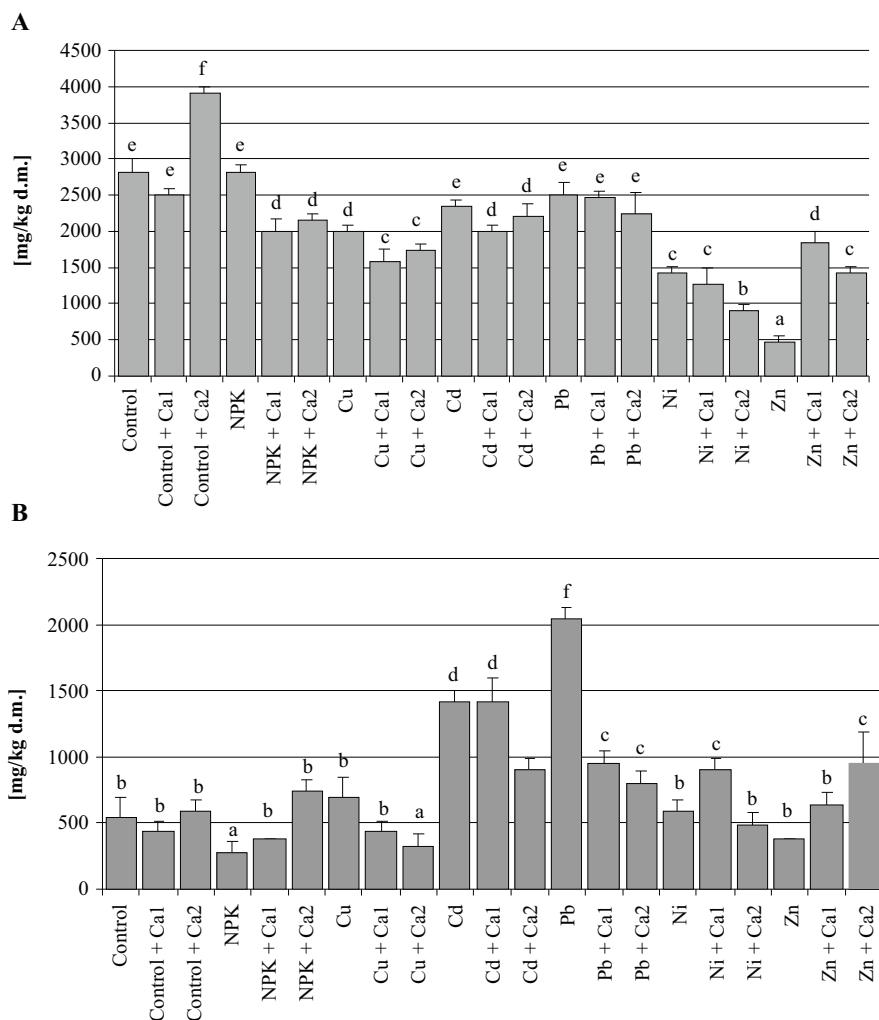


Fig. 1. Magnesium content in shoots (A) and roots (B) of broad bean (*Vicia faba* L., ssp. *major*) cultivated in unpolluted soil (Control, NPK) and in soil contaminated with single heavy metals and limed with a dose acc. to 1 Hh (...+Ca1) and acc. to 2 Hh (...+Ca2). Values marked with different letters are statistically different at $p = 0.05$

and nickel, liming (both with a dose computed acc. to 1 Hh and acc. to 2 Hh) apparently raised the Ca content in broad bean shoots. In the object with nickel contaminated soil the rise was almost twofold, while on the object with zinc contaminated soil – 20-fold. In the latter case Ca concentrations in broad bean shoots after applied liming approximated the level of this element in the control plants. Similarly as in the shoots, also in roots soil contamination with a majority of the analyzed heavy metals caused a decline in Ca content (Fig. 2B).

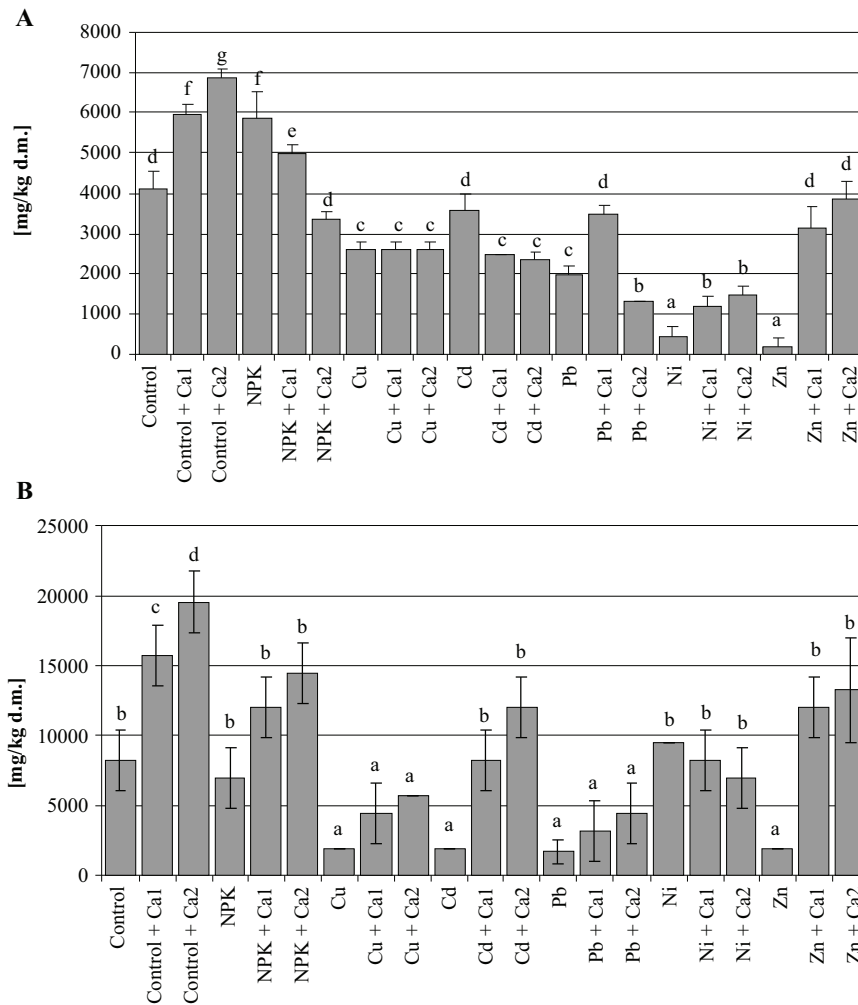


Fig. 2. Calcium content in shoots (A) and roots (B) of broad bean (*Vicia faba* L., ssp. maior) cultivated in unpolluted soil (Control, NPK) and in soil contaminated with single heavy metals and limed with a dose acc. to 1 Hh (...+Ca1) and acc. to 2 Hh (...+Ca2). Values marked with different letters are statistically different at $p = 0.05$.

On the other hand, application of liming usually caused an increase in the calcium content in these broad bean parts, which was the higher, the higher was the lime dose. In objects where the soil was contaminated with cadmium and zinc this measure contributed to increasing the Ca level in broad bean roots to the same one as in unpolluted plants. Only in the case of soil polluted with nickel no changes in the Ca content were registered in broad bean roots growing in it as an effect of liming, but the level of this

element did not differ significantly either from the calcium content in plants growing in natural soil. The Author's former studies showed that at joint application of all heavy metal doses the concentrations of this element in broad bean roots growing in contaminated and limed soil were also apparently higher in comparison with the roots growing in polluted soil but without liming [9].

Soil contamination with copper, lead and cadmium did not affect significantly the iron content in broad bean shoots (Fig. 3A). However, soil contamination with nickel and zinc caused a considerable (ca 3 –fold for Ni and 4-fold for Zn) increase in iron content. It was connected with a decrease in soil pH value in the objects polluted with these elements [6]. Solubility of iron compounds increases proportionally to the soil acidification degree. The iron content in plants changes considerably during the growing period. In legumes the content on the level of between 75 and 400 mg/kg d.m. is registered [10]. In conditions of nickel contaminated soil, the lime dose calculated acc. to 1 Hh caused further development of the Fe level in broad bean shoots, whereas the dose computed acc. to 2 Hh caused that the Fe level declined to the level noted in the control plants. In the case of zinc contaminated soil, a lower CaO dose decreased the iron content in broad bean shoots by ca 1/3, while the higher one led to a further decline to the level similar to the one registered in the control plants. No apparent differences in the iron content between unpolluted plants and those growing in Pb, Cu or Cd contaminated soil were registered either in broad bean shoots or roots (Fig. 3B). In these objects liming caused only slight fluctuations of the iron content in these plant parts. On the other hand, soil contamination with zinc affected a considerable, 6-fold decrease in the iron content in broad bean roots. Liming with a dose established on the basis of double hydrolytic acidity raised the content of this element to the level similar to the control plants. Similarly, in conditions of soil contamination with nickel, already the lime dose calculated according to single hydrolytic acidity raised the iron level in broad bean roots to the same as noted in the control plants, whereas a higher CaO dose caused a further increase in the Fe content in broad bean roots. In studies on the cooperation of NPK treatment with the liming effect on bioavailability of some metals to meadow plants, the most intensive iron bioavailability was registered in plants in objects where liming was used [11]. In some other research non-directional changes in the iron content in plants were observed irrespective of liming application [12, 13]. There is a considerable interrelation between the metabolic effect of iron and other trace metals. Excessive amounts of metals, particularly Mn, Ni and Co reduce the uptake and translocation of iron, which as a result inhibits chlorophyll formation leading to chlorosis. These interactions occur both in the soil environment and in plant tissues [14]. Such symptoms and a declined chlorophyll content were noticed in plants growing in zinc contaminated soil [15]. Proper calcium supply improved plant resistance to either deficiency or excess of iron [10]. Plants growing in zinc contaminated soil after liming application revealed a much better condition than those which were growing in polluted but non-limed soil (the Author's own unpublished data). A complex character of the antagonism in the Fe–Ca relation, which has been emphasized in literature, depends on different soil conditions and concerning the soil metabolism is sometimes combined with other elements [10].

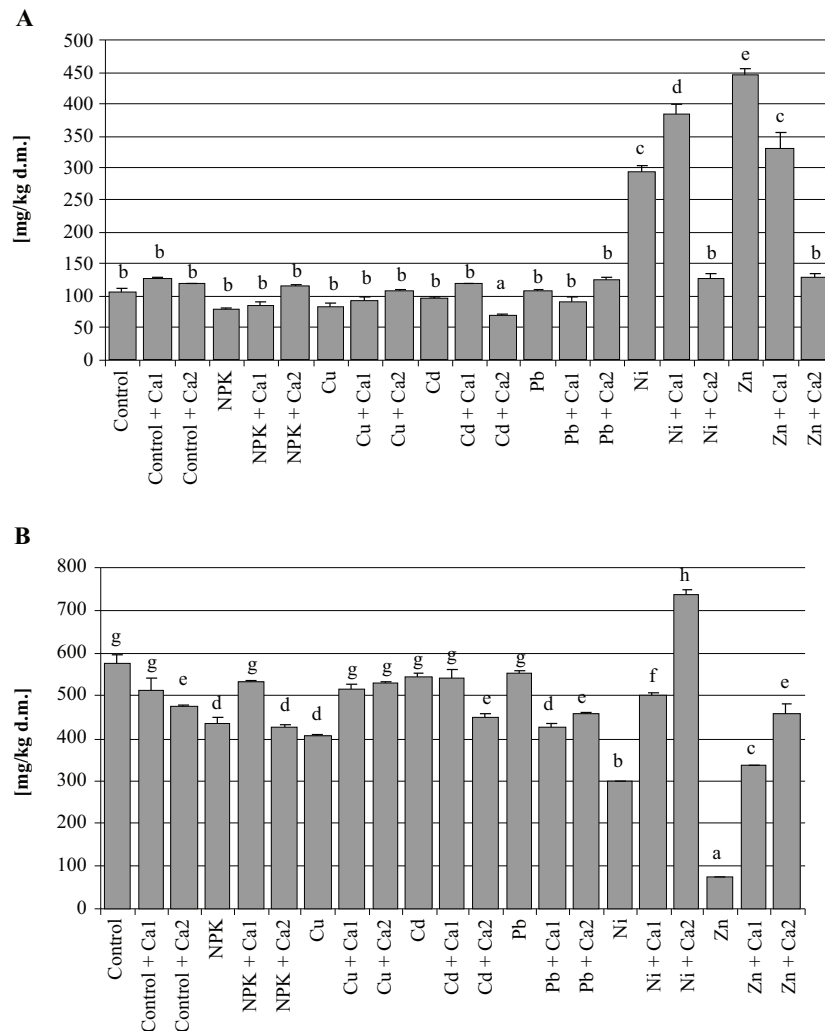


Fig. 3. Iron content in shoots (A) and roots (B) of broad bean (*Vicia faba* L., ssp. *maior*) cultivated in unpolluted soil (Control, Control +NPK) and in soil contaminated with single heavy metals and limed with a dose acc. to 1 Hh (...+Ca1) and acc. to 2 Hh (...+Ca2). Values marked with different letters are statistically different at $p = 0.05$.

Conclusions

1. Soil contamination with heavy metals, such as Cu, Cd, Pb, Ni and Zn causes significant changes of Ca, Mg and Fe contents in broad bean plants.
2. Application of liming contributes to balancing the contents of the analyzed elements in a plant. After liming the content of Ca, Fe and Mg in plants growing in soil

contaminated with individual heavy metals in most cases was on the level similar to the one registered in plants growing in unpolluted soil.

References

- [1] Gorlach E. and Curyło T.: Acta Agr. Silv. Ser. Agr. 1990, **29**, 83–92.
- [2] Siuta J.: Gleba, diagnozowanie stanu i zagrożenia. Wyd. IOŚ, Warszawa 1995.
- [3] Kabata-Pendias A. and Piotrowska M.: Ocena stopnia zanieczyszczenia gleb i roślin metalami ciężkimi i siarką. Wyd. IUNG Puławy, 1993, ser. P, 53 pp.
- [4] Gospodarek J.: Ecol. Chem. Eng. 2006, **13**(11), 1231–1240.
- [5] Gospodarek J.: Consequent effect of soil contamination with heavy metals on broad bean seed quality (*Vicia faba* L., ssp. *maior*), (Ecol. Chem. Eng. 2008, **15**(1–2), 55–64.
- [6] Gospodarek J. and Nadgórska-Socha A.: Ecol. Chem. Eng., 2006, **13**(6), 505–512.
- [7] Ostrowska A, Gawliński S. and Szczubiałka Z.: Metody analizy i oceny właściwości gleb i roślin. Katalog. Instytut Ochrony Środowiska. Warszawa 1991.
- [8] Azucue J. and Murdoch A.: Int. J. Environ. Chem., 1994, **57**, 151–162.
- [9] Jaworska M., Gospodarek J.: Ecol. Chem. Eng. 2005, **12**(8), 803–809.
- [10] Kabata-Pendias A. and Pendias H.: Biogeochemia pierwiastków śladowych, Wyd. Nauk. PWN Warszawa 1993.
- [11] Maciejewska M. and Kotowska J.: Fol. Univ. Agric. Stetin. 1998, **190**, Agr. (72), 205–209.
- [12] Scheffer K., Koch E. and Vardaskis F.: Landwirtsch. Forsch. 1978, **21**(3–4), 156–161.
- [13] Kotowska J.: Wpływ wapnowania i nawożenia mineralnego na plon oraz zawartość Cu, Zn, Fe, Ca, K, N, P w roślinach uprawianych w zmianowaniu. 1992, Rozprawy **146**, AR Szczecin, 85 pp.
- [14] Bergmann W.: Ernährungsstörungen bei Kulturpflanzen, 1988, 2nd ed. VEB G. Fisher Verlag, Jena, 762 pp.
- [15] Nadgórska-Socha A., Gospodarek J., Jaworska M. and Ciepał R.: Ecol. Chem. Eng., 2005, **12**(4), 421–426.

WPLYW WAPNOWANIA GLEBY SKAŻONEJ METALAMI CIĘŻKIMI NA ZAWARTOŚĆ MAGNEZU, WAPNIA I ŻELAZA W ROŚLINACH BOBU (*Vicia faba* L. ssp. *maior*)

Katedra Ochrony Środowiska Rolniczego, Uniwersytet Rolniczy w Krakowie
Katedra Ekologii, Uniwersytet Śląski w Katowicach

Abstrakt: Celem podjętych badań było określenie wpływu zróżnicowanych dawek wapna na zawartość manganu, wapnia i żelaza w roślinach bobu rosnących w warunkach gleby zanieczyszczonej pojedynczymi metalami ciężkimi na poziomie III stopnia zanieczyszczenia wg klasyfikacji IUNG. Analizie poddano bób (*Vicia faba* L., ssp. *maior*) odm. Windsor Biały uprawiany w dwóch seriach: na glebie wapnowanej i niewapnowanej. W każdej serii rośliny uprawiano w następujących obiektach: gleba niezanieczyszczona – o naturalnej zawartości metali ciężkich (Kontrola); gleba niezanieczyszczona – o naturalnej zawartości metali ciężkich nawożona mineralnie (NPK); gleba zanieczyszczona kadmem w dawce: $4 \text{ mg} \cdot \text{kg}^{-1} \text{ s.m.}$; gleba zanieczyszczona ołowiem w dawce: $530 \text{ mg} \cdot \text{kg}^{-1} \text{ s.m.}$; gleba zanieczyszczona miedzią w dawce: $85 \text{ mg} \cdot \text{kg}^{-1} \text{ s.m.}$; gleba zanieczyszczona cynkiem w dawce: $1000 \text{ mg} \cdot \text{kg}^{-1} \text{ s.m.}$; gleba zanieczyszczona niklem w dawce: $110 \text{ mg} \cdot \text{kg}^{-1} \text{ s.m.}$ Wapnowanie przeprowadzono na podstawie analizy kwasowości hydrolitycznej gleby z poszczególnych obiektów. Zastosowano dwie dawki: według 1 i 2 Hh. Dawki wapna wynosiły odpowiednio: Kontrola – 356 i 712 $\text{mg CaO} \cdot \text{kg}^{-1} \text{ s.m.}$; Kontrola + NPK – 420 i 840 $\text{mg CaO} \cdot \text{kg}^{-1} \text{ s.m.}$; gleba zanieczyszczona kadmem – 504 i 1008 $\text{mg CaO} \cdot \text{kg}^{-1} \text{ s.m.}$; gleba zanieczyszczona ołowiem – 420 i 840 $\text{mg CaO} \cdot \text{kg}^{-1} \text{ s.m.}$; gleba zanieczyszczona miedzią – 398 i 796 $\text{mg CaO} \cdot \text{kg}^{-1} \text{ s.m.}$; gleba zanieczyszczona cynkiem 860 i 1720 $\text{mg CaO} \cdot \text{kg}^{-1} \text{ s.m.}$; gleba zanieczyszczona niklem 524 i 1048 $\text{mg CaO} \cdot \text{kg}^{-1} \text{ s.m.}$

Skażenie gleby metalami ciężkimi, takimi jak Cu, Cd, Pb, Ni i Zn powoduje statystycznie istotne zmiany w zawartości Ca, Mg i Fe w roślinach bobu. Zastosowanie zabiegu wapnowania przyczynia się do zrównoważenia zawartości badanych pierwiastków w roślinie – po ich przeprowadzeniu zawartość Ca, Fe i Mg w roślinach rosnących w glebie skażonej poszczególnymi metalami ciężkimi w większości przypadków kształtują się na podobnym poziomie, jak w roślinach rosnących w glebie niezanieczyszczonej.

Słowa kluczowe: metale ciężkie, wapnowanie, akumulacja, Mg, Ca, Fe