

EFFECTS OF ACID LOADINGS ON HEAVY METAL MOBILIZATION IN CAMBISOLS

Szilárd Szabó, György Szabó, Árpád Bihari

*University of Debrecen Department of Landscape Protection and Environmental Geography, Debrecen,
Egyetem sq. 1. H-4032, Hungary
E-mail: szszabo@delfin.unideb.hu*

Szabó Sz., Szabó Gy., Bihari Á. EFFECTS OF ACID LOADINGS ON HEAVY METAL MOBILIZATION IN CAMBISOLS. *Annales Geographicae* 40 (2), 2007.

Abstract: Acidification can cause physical, chemical and biological degradation of the soils. This article deals with the chemical degradation and further with the acidic loads on heavy metal mobilization. Six heavy metals (Co, Cu, Fe, Mn, Ni, Zn) were examined in samples of Cambisol soil type. Acidic extraction experiment was carried out with different concentrations of HNO₃ and with different exposition time. The obtained results show that the order of mobility changes with acid concentration and exposition. One day and 1 mol loadings have significant effect on the heavy metal mobilization.

References 14. Figs 8. Tables 2. In English, summary in Lithuanian.

Keywords: pH, acid loading, heavy metal mobilization, mobilization order of heavy metals

Received: 12 June 2007, accepted: 20 September 2007.

Introduction

The key element of sustainable agriculture is the soil that is endangered by several degradation processes: erosion, acidity, compaction, extreme water balance, physical and biological degradation, reduction of the buffer capacity and different pollutions. Erosion and acidity affects the largest areas soils in this country. The present paper focuses on the acidity from the two main degradation processes.

Acidity of soils is unwanted both from agricultural and environmental points of views: nutrient content is reduced, physical properties become disadvantageous and cations important for the growth of plants are washed out. The pH of soils has an effect on the quality of the surface and subsurface waters and on the biological activity of the soils. Due to decreasing pH a new equilibrium is set on the surface of soil colloids therefore metals get into the soil solution: Al³⁺ ions acting as root poisons and heavy metals toxic in effect/quantity are mobilized (Csillag et al. 1998; Filep, Blaskó, 1997; Filep, Csillag, 1993; Várallyay, Láng, 2001; Blaskó, 1983).

Regarding landscape protection the mobilization of heavy metals – into a state that plants are able to uptake or their washing out into the groundwater – may cause problems in several aspects. It may endanger production potential just as it reduces settlement development possibilities and biodiversity (Csima, 1993).

Our study area is qualified as an arable land under intense cultivation not polluted by heavy metals. At certain areas significant soil acidity occurred due to natural and artificial processes. This resulted in the supposed solution of metals easy to mobilize by soil moisture. These metals were washed into deeper layers in the soil section by precipitation. Therefore deficiency can be detected regarding several metals rather than danger from surplus. Metals studied are essential trace elements. Their lack presents a problem not only in plant growing but in cattle breeding as well due to the low metal content of the fodder plants (Goulding, Blake, 1998; Szabó, 2000; O'Neill, 1993).

In the course of this work an acid loading experiment were carried out in the Cambisol of a study area in the Foreland of the Bükk Mountains (Fig.1.). In the course of this the effects of loadings by nitric acid of different concentrations and the effects of different exposition times on the dissolution of heavy metals were studied.

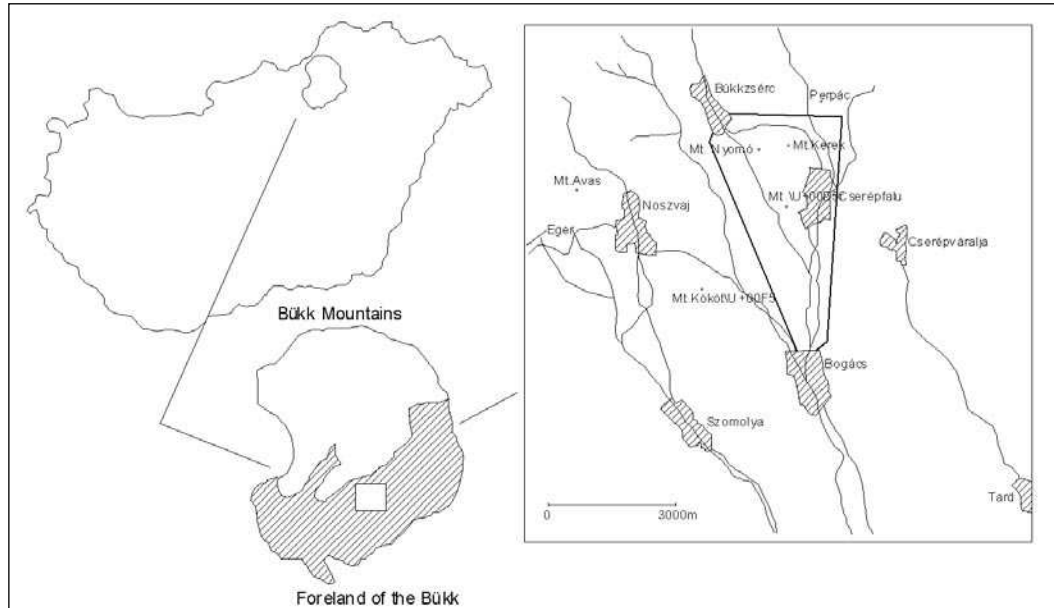


Fig 1. Situation of the sample area.

1 pav. Pavyzdžiū ėmimo teritorija.

1. Material and methods

Twenty soil samples (point sample) were taken for the examinations out of which 10–10 came from the Cambisols of arable lands and vineyards. Samples were taken from a depth of 0–25 cm. Acid extraction experiments were carried out on the soil samples. The total metal concentrations in the soil samples were determined and the mobilized amounts were compared with these values.

There are 39 soil types in Hungary and Cambisols are very widespread among them, their proportion is 10%. The main territory of them is close the chernozem soils (with more precipitation) in the hilly areas and Luvisols (with fewer precipitation) in the lee side drought basins of the mountains. Cambisols play a very important role in the agriculture in mountain areas, because their properties (humus content, pH etc.) are suitable for the plant production.

During the experiment, 5 g soil was extracted with 50 ml nitric acids of 0.01; 0.1; 1 and 10 M concentrations with 1 hour, 1 day and 1 week of exposition times. Heavy metal concentrations (Co, Cu, Fe, Mn, Ni, and Zn) were determined from the filtrates using F-AAS technique. The total metal concentration was determined according to the Hungarian Standard MSZ-08-1722:1989 by H₂O₂+HNO₃ digestion using F-AAS technique (Perkin-Elmer 3000). The digestion was carried out in 130°C temperature and standard barometric pressure environment with Gerthard SMA 2000 equipment. Triple repetitions were applied in the experiment.

Besides analysing metal contents the following soil base examinations were carried out: pH (1:2.5 suspension, H₂O and KCl), hydrolytic acidity (with 8.2 pH Ca-acetate), grain-size (Köhn pipe method), humus content (Tyurin method) and quality (Hargitai, 1993), CaCO₃ content (Scheibler type calcimeter) (Filep, 1999).

Statistical analysis of the results was started with studying normality and as it was found that most of the variants have no normal distribution Mann-Whitney test was applied in the analyses (Zar, 1995).

Concentrations measured in the filtrates were compared to the different concentrations of the acid loadings and to the different exposition times. Apart from these there was possibility to compare the dissolved heavy metal concentrations in soils taken from arable lands and vineyards.

2. Results and discussion

Properties of the soils

Table 1 lists the laboratory analysis results of the soil samples. These soil properties significantly influence metal bonding and mobilization.

Table 1. Results of the soil base examinations of the samples (average of 20 samples \pm standard deviation)

1 lentelė. Dirvožemio pasotinimo bazėmis tyrimų rezultatai (vidutiniškai 20 pavyzdžių \pm standartinis nuokrypis)

Soil property <i>Dirvožemio savybės</i>	Arable land <i>Ariama žemė</i>	Vineyard <i>Vynuogynų žemė</i>
pH (H ₂ O)	5.46 \pm 0.19	6.38 \pm 0.75
humus quantity %	3.2 \pm 1.0	2.37 \pm 0.9
humus quality	0.42 \pm 0.16	1.54 \pm 1.15
sand (2-0.02 mm) %	37.3 \pm 8.0	24.7 \pm 2.7
silt (0.02-0.002 mm) %	33.4 \pm 4.5	32.3 \pm 4.7
clay (<0.002 mm) %	29.3 \pm 8.6	42.9 \pm 4.9

As it can be observed there is significant difference in the soil properties in the aspect of land use: the difference is significant ($p < 0.05$) except for the silt. It was important to take all of the soil samples from Cambisols. The sampling sites were distributed in a small area therefore it is assumed that the difference developed in soils that had once similar properties is a result of different land-use (primarily the method of treatment).

Studying the mobility of the metals

Studying the consequences of soil acidity was carried out by two weaker (0.01 and 0.1 M) and two stronger (1 and 10 M) acids. The occurrence of the latter two can be associated with hazards and inaccurate industrial management (e.g. waste depositories with no insulation, leakage from mine pit heaps, et.).

Table 2 summarises heavy metal concentrations of the extracts obtained from the experiment and their detailed analysis follows.

Order of mobility

The first step of data analysis included determining the order of mobility with regard to the exposition times and the acids of different concentrations.

In the case of the 1 hour exposition iron (5 % – 10 M) mobilised the least while copper (38 % – 10 M) and cobalt (34 % – 10 M) mobilised the most (Fig. 2.). The order of mobility at the smallest acidity loading is the following: Fe<Zn<Mn<Cu<Ni<Co. This is slightly redrawn at the largest acidity loading: Fe<Zn<Ni<Mn<Co<Cu. It is visible that using stronger acids nickel and cobalt dissolves less while copper dissolves well.

In the case of the 1 day loading using the 0.01 M concentration the order presented above does not change significantly but different order is found when acids of 10 M concentration were used: Fe<Zn<Ni<Cu<Mn<Co (Fig. 3). The mobility of copper was

Table 2. REffect of the nitric acid treatments of different concentrations and the different exposition times on the mobilization of heavy metals in the soils (average of 20 samples, mg/kg)*. The first row shows the total metal content of the soil by elements.

2 lentelė. Įvairios koncentracijos natrio rūgšties poveikis sunkiųjų metalų kaupimuisi dirvožemyje esant įvairiam ekspozicijos laikui (vidutiniškai 20 pavyzdžių, mg/kg)*. Pirmoje eilutėje pateiktos bendrosios cheminių elementų koncentracijos dirvožemyje.

	Cu	Ni	Co	Zn	Mn	Fe
Soil Dirvožemis	24	34	15	53	1465	27460
1 hour exposition / Ekspozicijos trukmė 1 val.						
0.01M	0.9	1.8	1.3	1.0	49	7
0.1M	3.0	3.9	1.9	2.4	104	30
1M	8.9	6.1	3.0	4.7	200	431
10M	9.1	7.3	5.1	4.6	405	1402
1 day exposition / Ekspozicijos trukmė 1 diena						
0.01M	1.0	2.3	1.5	1.0	69	7
0.1M	3.9	5.9	3.0	4.1	222	250
1M	12.9	10.7	7.4	10.5	542	2942
10M	14.9	15.7	12.0	14.9	1012	6904
1 week exposition / Ekspozicijos trukmė 1 savaitė						
0.01M	0.4	2.4	2.1	1.1	103	5
0.1M	4.2	9.6	6.7	7.2	486	235
1M	14.6	18.4	14.2	19.6	1168	7037
10M	15.2	22.1	14.3	25.8	1329	12897

* Small differences can be caused by the measuring error of the applied F-AAS equipment / Nedideliu skirtumus galima paaiškinti matavimo paklaida naudojant F-AAS įrangą

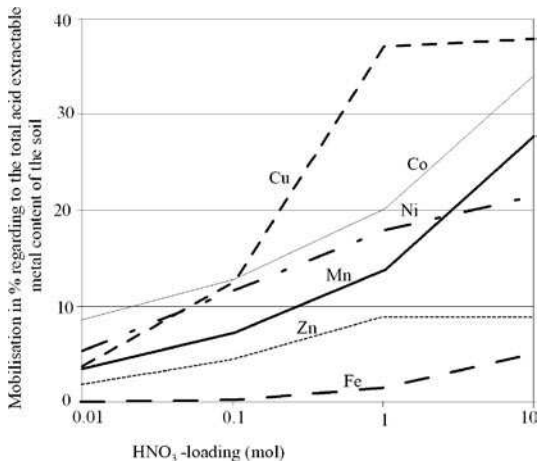


Fig 2. Effect of the 1 hour exposition time on metal content.

2 pav. 1 val ekspozicijos laiko poveikis metalų koncentracijai.

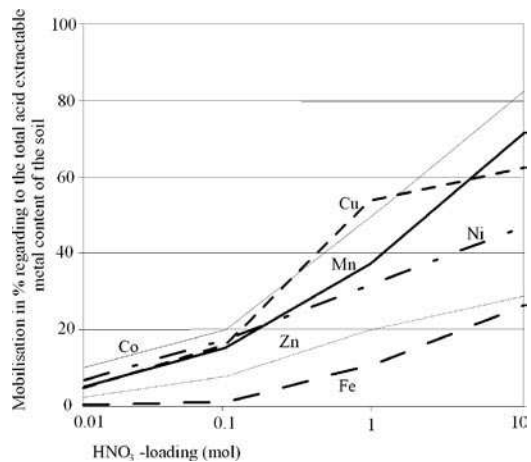


Fig 3. Effect of the 1 day exposition time on metal content.

3 pav. 1 dienos ekspozicijos laiko poveikis metalų koncentracijai.

reduced and cobalt gained the greatest mobility. The second most mobile is manganese. The quantities dissolved are greater especially in the case of the 10 M acidity loading: e.g. 80 % of the cobalt content of the soil gets into solution and five times the concentration of iron in the 1 hour loading moves into solution here.

The 1 week exposition modifies the order even at the smallest loading: $Fe < Zn \leq Cu < Ni \leq Mn < Co$ and it is not changed by the 10 M loading: $Fe \leq Zn < Cu \leq Ni < Mn < Co$. The quantity of the dissolved metals increases further as 95 % of the cobalt, 90 % of the manganese and even 47 % of the least mobile iron are mobilized (Fig. 4).

Effects of the exposition times

Significant differences were studied among the quantity of mobilized metals, the exposition times, the different concentrations of acidity loadings and the land-use.

The one hour and one day exposition times in general (co-interpreting the soils of the arable lands and the vineyards) had no significant effect at the smallest acidity concentration, however, at the more concentrated loadings exposition times has significant effect on metal dissolution. The explanation for this is that weaker acidity loadings mobilized such metal concentrations that were close to the detection limit and only longer exposition times or more concentrated acidity loadings produced detectable differences.

The situation is not so clear between the one day and one week exposition times (co-studying arable lands and vineyards). Significant difference was found at nickel, zinc and iron in the case of acids stronger than 0.01 M between the exposition times mentioned. In the case of cobalt and manganese significant difference was found at every acid loading comparing the amount of metals mobilized by the one day and one week exposition times.

Between one hour and one week exposition times, significant differences were detected in all possible cases.

The graphic gained from 4 points (according to acidity concentrations) is not enough for the exact describing of the extracted rates it is only informal. Generally the flattening out of the graphic is the least significant in the case of the zinc, the iron and the nickel thus here stronger acids have significant effects. In the case of the copper and cobalt, the nitric acid of 10 M concentration causes no significant concentration increase thus almost the total mobile rate of these elements is dissolved at the 1 M treatment, however, to reach this, different exposition times are required for the particular metals. This latter statement is only true for the 1 week treatment in the case of the manganese.

Effect of the concentrations

Mobility of the metals according to the acidity concentrations on the basis of exposition times was also studied.

It can be seen in the diagrams (Fig. 5–8.) that generally the mobilized quantity increases with the length of the exposition times in the case of most of the metals. Copper forms the exception as its concentration was reduced in the solution in the case of the 1 week extraction therefore re-bonding took place at the 0.01 M acidity loading.

In the cases of the cobalt, the nickel, the zinc, the manganese and the iron different exposition times significantly increase the quantity of the dissolving metals using stronger acids while in the case of the copper this increase is only significant at the 1 day treatment then only a minimum quantity is mobilised.

Variation analysis was performed among the concentrations of the acids as well regarding exposition times.

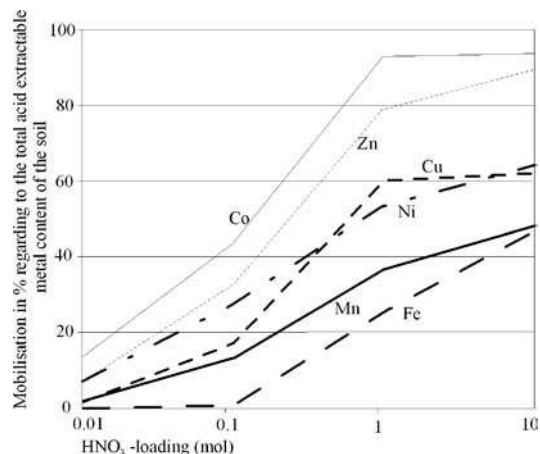


Fig 4. Effect of the 1 week exposition time on metal content.

4 pav. 1 savaitės ekspozicijos laiko poveikis metalų koncentracijai.

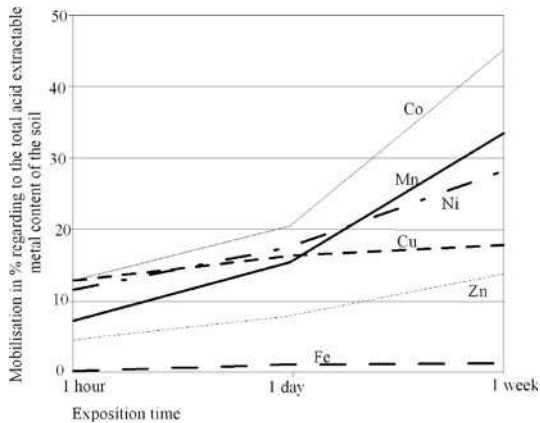


Fig 5. Metal mobilization using 0.01M nitric acid.
5 pav. Metalų kaupimasis paveikus dirvožemį 0.01 M koncentracijos azoto rūgštimis.

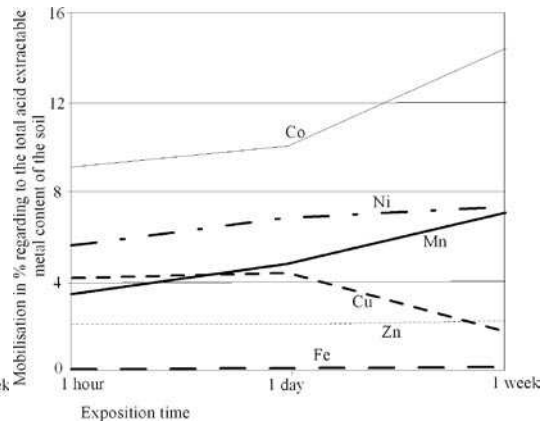


Fig 6. Metal mobilization using 0.1M nitric acid.
6 pav. Metalų kaupimasis paveikus dirvožemį 0.1 M koncentracijos azoto rūgštimis.

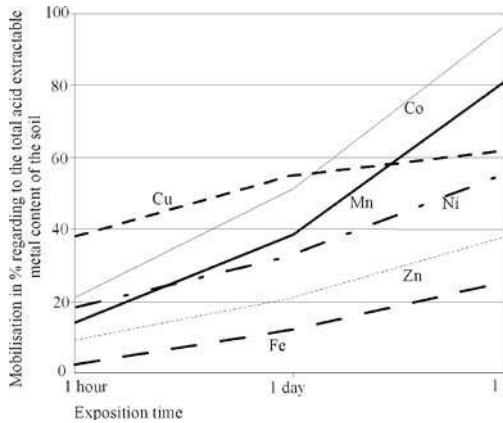


Fig 7. Metal mobilization using 1M nitric acid
7 pav. Metalų kaupimasis paveikus dirvožemį 1 M koncentracijos azoto rūgštimis.

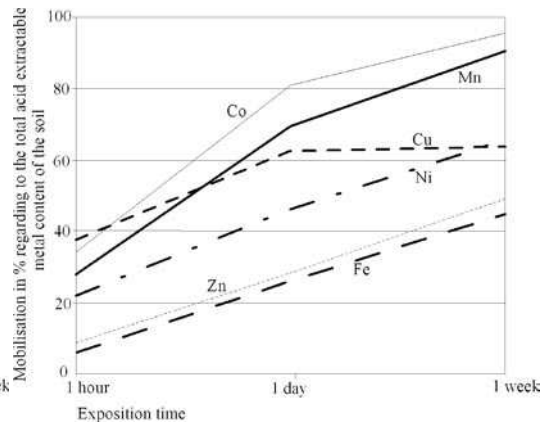


Fig 8. Metal mobilization using 10M nitric acid
8 pav. Metalų kaupimasis paveikus dirvožemį 10 M koncentracijos azoto rūgštimis.

The difference between the 0.01 M and the 0.1 M acidity loadings is significant in all of the cases. If the samples of the vine yards and the arable lands are studied separately there are no significant differences.

Similarly significant difference is observed in all of the cases between the 0.1 M and 1 M acidity loadings and there is no change if the land use is taken into consideration.

Between the 1 M and 10 M treatments the relationship is not so clear. Generally there is no significant difference between the mobilized concentration of copper (one hour and one week exposition), cobalt (one week) and zinc (one hour) but in each other cases there is. The samples of the vineyards have the same tendencies. In the case of the arable lands there is no difference between the mobilization of copper, nickel and zinc (one hour exposition) and cobalt (one week exposition).

At 0.01 M acid exposition times have significant effect in the case of the cobalt and the manganese especially the 1 week treatment increases the mobilized concentration. At 0.1 M; 1 M and 10 M treatments exposition times are important in the cases of all of the metals except for the copper. Similarly to the 0.01 M treatment the 1 week exposition time has the determinative role. Most of the copper, however, is mobilised within 1 day. 10 M nitric acid dissolves significant amount of metals even within 1 day but further quantities are mobilized in the case of the 1 week treatment.

Conclusions

The mobility of the studied metals is greatly influenced by the length of the exposition time. Due to the acidity of the soils the concentration of those metals the adsorption of which is largely dependant on pH (Cu, Ni, Zn) is smaller as they were washed out into the bottom part of the soil. Apart from this, cultivation also contributes significantly to the impoverishment of the soil in micro-elements. Therefore the easily mobilized rate of the metals is reduced naturally resulting in mobility orders in the experiment that are in opposition to the literature (Csillag et al. 1994; Kiekens, Cottenie, 1985): the suggested mobile manganese and cobalt frequently preceded copper, zinc and nickel that are regarded as more mobile metals in the literature (in the cited references sewage sludge and metal-enriched samples were used). Iron remained the least mobilizing element in all of the cases.

Considering acids of different concentration in the cases of zinc, nickel and iron the effect of the 10 M acid is great while most of the copper, cobalt and manganese are mobilized already at the 1 M acid treatment.

Regarding the effects of the exposition times, 0.01 M acid treatment should be separated – where only the cobalt and the manganese were mobilised with one week exposition time – and the 0.1-1-10 M treatments where only the mobility of the copper were not influenced significantly by the exposition time.

References

- Blaskó, L.** 1983. Relationship between the acid or over limed condition of the soil and phosphorous supply in meadow soils (in Hungarian). *Agrokémia és Talajtan*. Vol. 32 No. 3–4 p. 399–406.
- Csillag, J., Lukács, A., Bujtás, K., Németh, T.** 1998. Impact of soil contamination and acidification on heavy metal concentration in the soil solution. *Soil Pollution; Soil, Water and Environment Relationships*. G., Filep (Eds.), Debrecen: DATE, p. 65–73.
- Csillag, J., Lukács, A., Molnár, E., Bujtás, K., Rajkai, K.** 1994. Study of Heavy Metal Overloading of Soils in a Model Experiment. *Agrokémia és Talajtan*, No. 43. p. 196–210.
- Csima, P.** 1993. General landscape protection and nature protection. (in Hungarian) *Öko* Vol. 4. No. 2–3. p. 12–18.
- Filep, Gy., Blaskó, L.** 1997. The role of amelioration in agricultural land use. *Land Use and Soil Management* G., Filep, T., Németh (Eds.), Debrecen: DATE, p. 68–85.
- Filep, Gy., Csillag, J.** 1993. Aluminium Mobilization as an Aspect of Chemical Degradation of the Soil. *Agrokémia és Talajtan*, No. 42 (1-2), p. 79–88.
- Filep, Gy.** 1999. Soil chemistry. Budapest: Akadémiai Kiadó 330 p.
- Goulding, K. W. T., Blake, L.** 1998. Land use, liming and the mobilization of potentially toxic metals. *Agriculture, Ecosystems and Environment*, No. 67, p. 135–144.
- Hargitai, L.** 1993. The role of organic matter content and humus quality in the maintenance of soil fertility and in environmental protection. *Landscape and Urban Planning*, No. 27. p. 161–167.
- Kiekens, L., Cottenie, A.** 1985. Principles of investigation on the mobility and plant uptake of heavy metals. *Chemical methods for assessing bio-available metals in sludges and soils*. R., Leschber, R., D., Davis, P., L'Hermite (Eds.), London – New York: Elsevier Applied Science Publishers, p. 32–41.
- O'Neill, P.** 1993. Environmental chemistry, London-Glasgow-New York-Tokyo-Melbourne-Madras: Chapman and Hall, 268 p.
- Szabó, Gy.** 2000. Geographical investigation of the heavy metal content of the soils and plants in a study area in the Foreland of the Bükk Mountains (in Hungarian). *Studia Geographica, Institutum Geographiae, Universitas Debreceniensis*, No. 8. 144 p.
- Várallyay, Gy., Láng, I.** 2001. The double function of the soil: natural resource and a habitat (in Hungarian). *Acta Agraria Debreceniensis*, p. 5–19.
- Zar, J. H.** (1995). *Biostatistical Analysis*, Prentice-Hall International Edition, 718 p.

Szilárd Szabó, György Szabó, Árpád Bihari

Debreceni universitetas, Vengrija

Rūgščių poveikis sunkiųjų metalų kaupimuisi smėlio dirvožemiuose

Santrauka

Aplinkos ir dirvožemių rūgštingumas yra ne tik nacionalinė bet ir tarptautinė problema. Rūgščių poveikyje pablogėja dirvožemių fizinės, cheminės ir biologinės savybės, o tai sukelia kitas nepageidaujamas pasekmes (sumažėjusį derlingumą, sunkiųjų metalų susikaupimą ir pan.). Rūgščių poveikyje sunkieji metalai tirpsta. Tirpimo greitis priklauso nuo rūgščių koncentracijos ir ekspozicijos trukmės.

Šiame darbe analizuojamas Co, Cu, Fe, Mn, Ni ir Zn kaupimosi greitis dirvožemyje paveikus jį azoto rūgštimi. Panaudotos azoto rūgšties koncentracijos buvo 0.01; 0.1; 1 ir 10 M, o ekspozicijos laikas – 1 valanda, 1 diena ir 1 savaitė. Buvo tiriami poveikio skirtumai esant įvairioms rūgšties koncentracijoms ir ekspozicijos laikui.

Paaiškėjo, kad tirtųjų metalų kaupimosi greitis priklauso ir nuo rūgšties koncentracijos ir nuo ekspozicijos laiko. Mūsų nustatyta metalų kaupimosi greičio eilė skiriasi nuo pateiktosios kituose literatūros šaltiniuose, kadangi tirtuosiuose dirvožemio pavyzdžiuose metalų koncentracijos buvo mažesnės. Lengvai besikaupiantys metalai (Cu, Zn, Ni) dėl natūralaus dirvožemio rūgštingumo buvo ištirpę dar prieš imant dirvožemio pavyzdžius. Tuo galima paaiškinti Co ir Mn pirmavimą kaupimosi greičio eilėje.