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Contents of nickel, zinc, copper and lead in agricultural soils of the plains in the northwestern part of the Republic of Srpska

Dijana Mihajlović[1], Svetlana Antić-Mladenović[2], Dragoja Radanović[1,3],Tihomir Predić[4], Mladen Babić[1], Sretenka Marković[1], Zoran Maličević[1]

[1]*Faculty of Agriculture University of Banja Luka*
[2]*Faculty of Agriculture University of Belgrade*
[3]*Institute for Medical Plant Research "Josif Pančić", Belgrade*
[4]*Agricultural Institute of Republic of Srpska, Banja Luka*

Summary

This paper presents the results and methodology of investigation conducted on agricultural soils of the plains in the northwest Republic of Srpska, aiming to determine the extent of heavy metals contamination: nickel (Ni), zinc (Zn), copper (Cu) and lead (Pb). The investigation included 140 soil samples from 14 sites, where the soil samples were taken on 5 locations, from two layers (depths): arable (0-25 cm) and sub-arable (25-50 cm). The total contents of metals were determined by a method of atomic spectrophotometry after acid digestion (HNO_3+H_2O_2). Organic matter content, CEC and pH were determined by standard agrochemical methods. The total contents of nickel in 78.5% of investigated soil samples were higher than the maximum allowed in the unpolluted soils (50 mg/kg). In 22.86% of the analysed samples, the content of zinc was higher than the maximum allowed in the unpolluted soils (100 mg/kg), while the content of copper and lead in the small number of samples was higher than the allowed maximum. Acidic soil reaction (pH<5.5) that increased bioavailability of metals was found in 38.6% of the samples investigated. A high degree of correlation was determined between the total content of certain metals (Cu and Ni, Cu and Zn). This suggests their common origin in the investigated area. The average contents of investigated metals in different layers (depths) were slightly different, having determined higher concentrations of Ni and Cu in the sub-arable layer that indicated the dominance of natural, geochemical sources of these metals in the soils. Territorial distribution of samples with high content of Ni and Zn corresponds to geological substrates which include minerals- natural carriers of Ni and Zn. This also indicates probable geochemical origin of these elements in the investigated soils. High contents of metals and acid soil reaction

indicate that it is necessary to continue research in order to determine the risk of increased transfer of heavy metals from soil to the crops grown.

Key words: heavy metals, soil, total content of metals

Introduction

Intensive technological development, industrialisation and urbanisation which are some of the main characteristics of the 20th century, were followed by the emission of large quantities of various hazardous and toxic substances into the environment. Among these substances, heavy metals (trace elements) have special impact on the environment. Those elements are involved in natural biological and geochemical processes and cannot be degraded or destroyed. Because of this, they pose one of the most important ecological risks. Some of these are essential elements, important for normal biological functioning of plants, animals and humans (e.g. Cu, Ni, Zn, Mn) while the others are not so essential or they are even considered toxic (e.g. Pb, Hg, As and Cd). Their presence in the soil in concentrations higher than maximum allowed for agricultural lands can cause various adverse effects (e.g. reduction or absence of the crops' yield, bioaccumulation in the food chain, movement through the environment etc.). Because of their potential risk on human health, U.S. Environmental Protection Agency (U.S. EPA) declared Pb, Cr, Ni, Zn, As, Cd, Cu, Hg, Sb, Be, Se, Ag, and Tl as ones of the most dangerous toxic substances (NCR, 2003).

The plains in the north-west part of the Republic of Srpska represent an important agricultural region of our country. In this area, the largest urban and industrial centres are located as well. In the valleys of the Una, Sana, Vrbas, Sava, Bosna, and Ukrina rivers, fertile alluvial soils, mainly used as agricultural land, developed on the bedrock formed in quaternary period.

These soils are formed by deposition of sediments that are brought with the river flow, creating soil layers with different chemical and physical characteristics. The origin of these sediments in the investigated plains is related to special rocks as well as to dolomite, limestone, flysh, peridotite and serpentinite *(Đerković et al., 1975, Mojičević et al.,1976, Laušević et al., 1982, Šparica et al., 1983, Sofilj et al., 1984, Šparica et al., 1986, Jovanović and Magaš, 1986).*

Numerous studies worldwide indicate that heavy metals contamination is highly pronounced in the soils near rivers which are often exposed to different anthropogenic influences that in addition with natural factors (alluvial and deluvial processes) determine the overall contents of metals *(Overesch et al., 2007, Ibragimow et al., 2010, Martin, 2000, Qishalaqi and Moore, 2007).*

Considering all the mentioned facts, the main objective of the paper was to determine the extent of contamination in the soils of the plains in the north-west part of the Republic of Srpska with specific heavy metals, i.e. nickel, zinc, copper and lead.

Material and methods

This research was carried out on agricultural soils of the plains in the north-west part of the Republic of Srpska and included 140 soil samples from 14 sites (Table 1.). The soil samples were taken at 5 locations, from two layers (depths): arable (0-25 cm) and sub-arable (25-50 cm). Sampling was carried out with the agrochemical probe forming the average sample for each depth (layer). During the process of sampling, the information relevant to description of micro locations (use of agricultural land, cultivated crops, and distance from the water stream, major roads and industrial facilities, GPS coordinates) were recorded.

The average soil samples were air dried, crushed and sieved to a particle size < 2mm. Main chemical properties of the soils were determined in these samples according to standard agrochemical methods: 1. Acidity (pH) measured in deionised water and 1M KCl, 2. Content of carbonates ($CaCO_3$) with Scheibler calcium-meter, 3. Organic matter content applying the method by Tjurin, 4. Cations exchange capacity with 1M NaAc (pH=7).

Total contents of metals were determined by the atomic spectrophotometry method after acid digestion with concentrated HNO_3 in addition of 33% solution of H_2O_2 *(Krishnamurty et.al., 1976)*. This is one of the basic methods for determination of the total metal content in soils according to which the maximum allowed concentrations of heavy metals in agricultural soils are given in the legislation of numerous countries as well as in the scientific literature *(Kabata-Pendias and Pendias, 1992)*.

Nitric acid neither causes degradation in the crystal lattice of the silicate minerals nor releases metals built in the crystal structure. The content of metals obtained after digestion with nitric acid is actually a pseudo-total content, and will be considered further as the total content.

Assessment of the degree of soil contamination with heavy metals (Pb, Ni, Zn and Cu) has been done by: 1. Comparison of their total contents in the investigated soils with the maximum allowed content for unpolluted soils, 2. Determination of the correlation degree between the contents of the same chemical elements at different depths, 3. Determination of the correlation degree between the contents of different chemical elements at the same depths 4. Estimation of the expected mobility and availability of metals based on main soil properties that were influenced by the available content of heavy metals in these. Statistical analysis was calculated using the Microsoft software package (Excel).

Tab. 1. The review of the sampling places

Pregled mjesta gdje su uzimani uzorci

Mark	Location	The sampling area
NT1	the Vrbas river valley	the field of Lijevče, route Aleksandrovac-Dubrave
NT 2	the Sana river valley 1	the field of Prijedor, route Omarska-Trnopolje
NT 3	the field of Cerovljani	the plateau of Cerovljani
NT 4	the Una river valley 1	route Dubica-Draksenić-Jasenovac
NT 5	the Una river valley 2	route Novi Grad-Kostajnica
NT 6	the Sana river valley 2	the field of Prijedor, route Prijedor-Sanski Most
NT 7	the Ukrina river valley 1	route Prnjavor-Derventa
NT 8	the Ukrina river valley 2	route Derventa-Brod
NT 9	the Bosna river valley 1	route Doboj-Podnovlje
NT 10	the Bosna river valley 2	route Modriča-Podnovlje
NT 11	the Bosna river valley 3	route Modriča-Miloševac- Crkvina
NT 12	the Sava river valley 1	the nearby of the Šamac
NT 13	the Sava river valley 2	the nearby of the Brod
NT 14	the Sava river valley 3	route Gradiška-Srbac

Results and discussion

Main chemical properties of the investigated soils

Investigated soils show great heterogeneity regarding the main chemical properties (Table 2.), which is mainly a consequence of specific features of their pedogenesis. Considering the individual samples, it is noticeable that they belong to different acidity range, from strongly acidic to alkaline soils *(Džamić et al.)*. However, there is obvious dominance of the acidic and moderately acidic soils (63.6% among the tested soil samples with pH<6.5), compared with soils with neutral (30.7%) and alkaline soil reaction (5.7%).

Tab. 2. Main chemical properties of the investigated soils (mean, standard deviation and range)

Glavne hemijske karakteristike ispitivanih zemljišta (srednja, standardno odstupanje i raspon)

Soil layer (the depth)	**pH 1M KCl ($t=25^0C$)**	**pH H_2O ($t=25^0C$)**	**$CaCO_3$ (%)**	**Organic matter (%)**	**CEC (meq/100g)**
Arable layer (0-25 cm)	5,95±1,02 (3,95-7,37)	7,06±0,92 (5,13-8,24)	2,76±6,43 (0,0-33,10)	1,66±0,51 (0,70-3,40)	20,46±8,70 (9,75-49,75)
Sub-arable layer (25-50cm)	5,98±1,06 (3,96-7,44)	7,16±0,90 (5,10-8,30)	2,86±6,65 (0,0-34,60)	1,49±0,46 (0,60-2,60)	19,91±7,90 (8,00-44,50)

Strong acidic soil reaction (pH<5.5), which increases the bioavailability of metals, was measured in 38.6% of investigated samples. Strong alkaline reaction and high content of carbonates were determined in the soil samples from the Sana River valley. Those characteristics are due to the river flow through rocks of the dolomite and lime stones. There is evidently a huge percentage of non-carbonate soils (more than 70%) among other analysed soil samples.

According to the determined content of organic matter (humus), the investigated soils belong to the group of moderately humus soils *(Jakovljević et al., 1995).* Opposite the soil pH-reaction and content of carbonates, the content of organic matter has decreased with the soil depth due to the presence of root mass and crop residues in the topsoil.

Homogenous content of organic matter in the investigated soils can be explained by the fact that the sampling was carried out on arable land covered by the same dominant crops (e.g. corn, wheat, clover) which involved similar agricultural practices.

The variation range of the determined cations exchange capacity (CEC) in the investigated soils is wide, probably caused by differences in their mechanical structure. In 70% of the investigated soil samples, CEC was moderate (12-25 meq/100g), while in 20% of the investigated samples was high (>25 meq/100g). The results indicate high capacity and affinity of the soil for metal ions adsorption *(Hazelton and Murphy, 2007)*. The higher values of CEC are found mainly in the samples with high content of organic matter.

Total contents of nickel, zinc, copper, and lead

In 78.57% of the investigated soil samples, the determined contents of nickel (Ni) were higher than the maximum allowed for unpolluted soils (50 mg/kg), whereas in 40% of these samples the content of Ni was 2-4 times higher than the maximum allowed (Figure 1.).

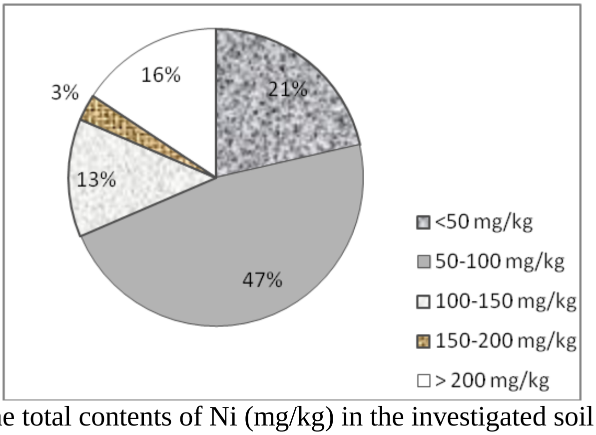


Fig. 1. The total contents of Ni (mg/kg) in the investigated soil samples
Ukupni sadržaj Ni (mg/kg) u ispitivanim uzorcima zemljišta

The highest content of Ni was found in the soils beside the Bosna and Ukrina Rivers, probably caused by the presence of peridotite and serpentinite rocks, which are natural carriers of Ni. Decomposition of primary minerals has led to Ni leaching from those rocks to the soils in the lower part of the river valley. In the previous research, it was concluded that higher contents of Ni in the soils from the lower part of the Vrbas River valley were due to a long term process of leaching this metal from the deposits of peridotite and serpentinite. This metal was leached mainly by Vrbas River tributaries *(Novković et al., 2008)*. The average total contents of Ni in the investigated soils from different depths show homogenous vertical distribution of this element (Table 3.). This is a confirmation of the assumption that the origin of Ni is determined by geochemical (natural) sources rather than by anthropogenic sources *(Soon and Abboud, 1990, Antić-Mladenović, 2004)*.

Tab. 3. Total contents of nickel, zinc, copper and lead in the investigated soil samples (mean, standard deviation and range)
Ukupni sadržaj nikla, cinka, bakra i olova u ispitivanim uzorcima zemljišta (srednja, standardno odstupanje i raspon)

	Ni (mg/kg)	**Zn (mg/kg)**	**Cu (mg/kg)**	**Pb (mg/kg)**
Arable layer (0-25 cm)	96,15±67,35 (25,00-291,20)	81,32±24,42 (49,30-170,30)	22,03±8,09 (8,90-42,90)	31,20±12,21 (13,60-100,80)
Sub-arable layer (25-50cm)	97,58±69,40 (25,30-294,70)	79,24±21,91 (46,70-135,40)	22,50±9,55 (9,70-64,80)	31,20±12,21 (10,20-52,20)
Maximum allowed contents*	50	100	60	100

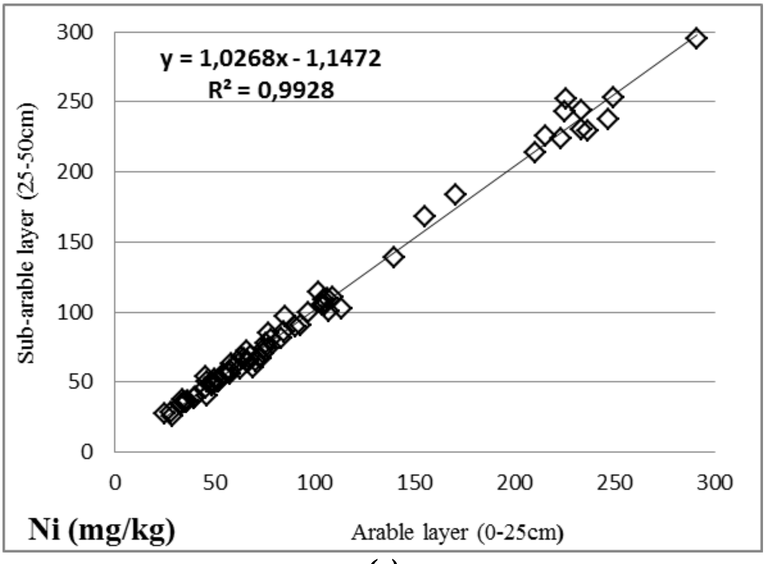
**Kabata-Pendias and Pendias (1992): Critical concentration of total metal content in the soil which could have toxic impact on plants*

This theory is confirmed by the linear regression equation between the contents of Ni in arable and sub-arable layer of the soil profile (Figure 2, a). Statistically high significant correlation has been determined between the total content of Ni in the layer 0-25 cm and 25-50 cm ($r = 0.99^{**}$). According to *Zhang et al. (2002)*, this indicates that Ni in the soils of the plains in the north-west part of the Republic of Srpska dominantly originates from geochemical sources.

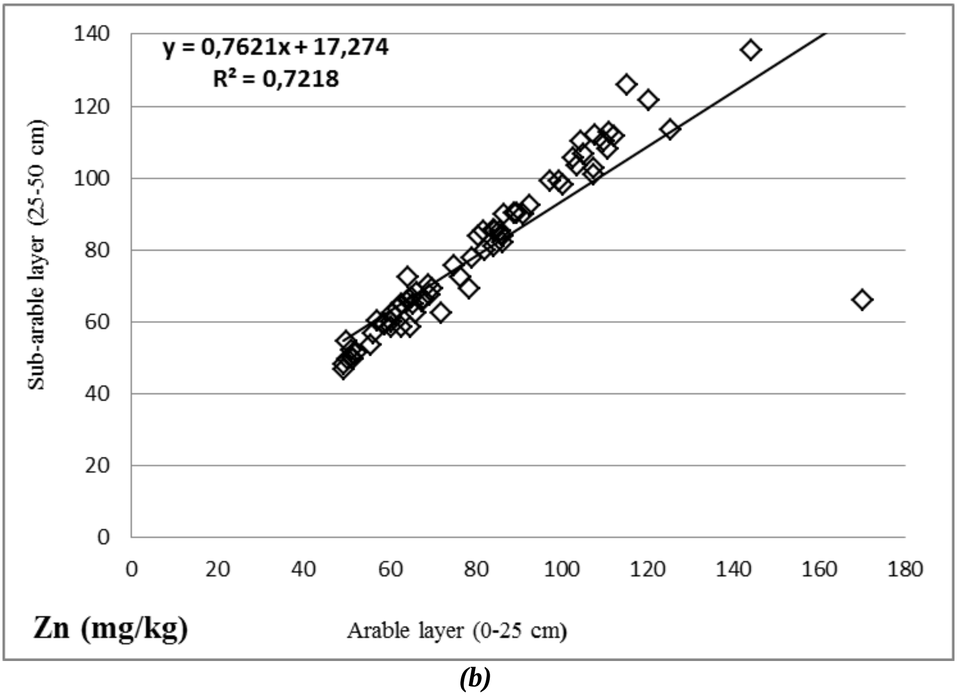
Tab. 4. Correlation coefficients between the contents of the Ni, Zn, Cu and Pb in investigated soils
Koeficijenti korelacije između sadržaja Ni, Zn, Cu i Pb u ispitivanim zemljištima

Metal	**Arable layer (0-25 cm)**			**Sub-arable layer (25-50cm)**		
	Ni	**Zn**	**Cu**	**Ni**	**Zn**	**Cu**
Zn	0,35**	1,00		0,48**	1,00	
Cu	0,75**	0,63**	1,00	0,69**	0,72**	1,00
Pb	NS	0,31**	0,25*	0,43**	0,77**	0,60 **

**statistically significant on the level of 0,01
* statistically significant on the level of 0,05



(a)



(b)

Fig. 2. XY-diagram showing the relation between total content of Ni (a) and Zn (b) in the layer 0-25 cm and 25-50 cm
XY dijagram koji pokazuje odnos između ukupnog sadržaja Ni (a) i Zn (b) u sloju 0-25 cm i 25-50 cm

The Zn content was higher than the maximum allowed (100 mg/kg) in 22.86% of the analysed soil samples, while the contents of Cu and Pb were higher in a small number of soil samples than the allowed values for these elements (Table 3.).

Territorial distribution of the samples with increased contents of Ni and Zn was similar, directly indicating the same or similar origin of those metals. Regarding the Zn content, it is evident that its vertical distribution is homogenous (Table 3). Together with the linear regression equation between the total content of Zn in different soil layers (Figure 2, b), this fact indicates the dominance of natural geochemical sources of this element in the area under examination.

NS statistically not significant

Mutual correlation coefficients between the total content of the heavy metals analysed in the investigated soils (Table 4.) indicate a strong linear relationship among the content of Ni and Cu, Cu and Zn in both soil layers analysed ($r \approx 0.7$). According to the research done by Reimann et al. (2001), statistically significant correlation coefficients among the content of the same elements between different soil layers refer to their common origin from geochemical sources.

Conclusion

The results of the investigation carried out on the soils in the north-west part of the Republic of Srpska showed the following: 1. In 78.7% and 22.86% of the analysed soil samples, the total contents of Ni and Zn were determined to be higher than the maximum allowed for unpolluted soils. 2. The total contents of Cu and Pb were within the allowed range, with the exception of few individual samples, 3. Vertical distribution of Ni, Cu and Zn in the soils from the examined area was homogenous, 4. The correlation between the content of Ni and Cu, Cu and Zn, Ni and Zn in different soil depths (0-25 and 25-50 cm) was statistically significant. Together with the previous conclusion, this indicates predominant origin of these metals from natural geochemical sources but does not exclude influence of anthropogenic sources. 5. The higher content of Ni and Zn, as well as high acidity and moderate adsorption capability of the soil suggest that it is necessary to provide additional investigation in order to determine the part of the total content of Ni and Zn which is bioavailable. In regards with these results, it is possible to get useful information about the impact of Ni and Zn on the environment, and to estimate their influence in the examined area.

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Садржаји никла, цинка, бакра и олова у пољопривредним земљиштима равничарског дијела сјеверозапада Републике Српске

Дијана Михајловић[1], Светлана Антић-Младеновић[2], Драгоја Радановић[1,3], Тихомир Предић[4], Младен Бабић[1], Сретенка Марковић[1], Зоран Маличевић[1]

[1] *Пољопривредни факултет Универзитета у Бањалуци*
[2] *Пољопривредни факултет Универзитета у Београду*
[3] *Институт за проучавање љековитог биља "Јосиф Панчић", Београд*
[4] *Пољопривредни институт Републике Српске, Бањалука*

Резиме

У овом раду су представљени резултати и методологија истраживања проведеног на пољопривредним земљиштима равничарског дијела сјеверозападне Републике Српске, чији је циљ био утврђивање степена загађености земљишта тешким металима: никлом (Ni), цинком (Zn), бакром (Cu) и оловом (Pb). Истраживањем је обухваћено 140 узорака са 14 локација, на којима је земљиште узорковано на пет микролокација из два слоја (дубине): ораничног (0-25 cm) и подораничног (25-50 cm). Укупни садржаји метала одређени су методом атомске апсорпционе спектрофотометрије, након киселинске дигестије (HNO_3+H_2O_2). Стандарним агрохемијским методама одређени су pH, садржај органске материје и капацитет за адсорпцију катјона у земљишту. Утврђени укупни садржаји никла су у 78,57% испитаних узорака виши од максимално дозвољеног садржаја за незагађена земљишта (50 mg/kg). У 22,86% анализираних узорака утврђен је садржај цинка виши од максимално дозвољеног (100 mg/kg), док је садржај бакра и олова у малом броју узорака виши од максимално дозвољеног. Кисела реакција земљишта (pH<5,5), која може да утиче на повећану биоприступачност метала, измјерена је у 38,6% узорака. Утврђен је висок степен корелације између укупних садржаја појединих метала (Cu и Ni, Cu и Zn), што упућује на њихово заједничко поријекло на испитиваном подручју. Установљене су приближно исте просјечне концентрације метала у оба испитивана слоја земљиша, што указује на доминантан природни, геохемијски извор тих метала на испитиваном терену. Територијални размјештај узорака са повишеним садржајима Ni и Zn одговара геолошким подлогама у чијем се минералном саставу јављају минерали – природни носиоци Ni и Zn, што такође упућује на вјероватно геохемијско поријекло поменутих елемената у земљишту. Високи садржаји неких метала и кисела реакција земљишта упућују на неопходност додатних испитивања, да би се утврдио степен ризика од њиховог могућег повишеног трансфера из земљишта у гајене културе.

Кључне ријечи: тешки метали, земљиште, укупни садржај метала

Dijana Mihajlović
E-mail Address:
dijana.mihajlovic@agrofabl.com