



## The effects of some agrotechnical measures on the uptake of nickel by maize plants

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**Abstract:** Nickel is a non-essential element in the nutrition of the majority of plant species and can be toxic to plants when its concentration in soils is high. Several soil properties have an effect on the uptake of this heavy metal by plants. The purpose of this investigation was to determine the effect of fertilization, soil acidification and liming on the uptake of Ni by maize plants grown on some alluvial soils. A pot experiment with maize plants grown on soils having various properties and elevated content of Ni was set up. The experiment lasted six weeks. The roots and shoots were analyzed for the concentration of Ni. From the results of the experiment, it can be concluded that the roots had higher concentrations of Ni than the shoots. The addition of mineral fertilizers (without application of other measures) mainly decreased the concentration and uptake of Ni by the roots and the transport of Ni to the shoots. Soil acidification (to pH 4.5) caused an increase in the Ni concentration in the plants and in its removal from the soil. Liming of acid soils had a positive effect on the uptake of Ni by young maize plants. The obtained results are important from the standpoint of reducing the pollution of plants by potentially toxic heavy metals.

**Keywords:** agrotechnical measures; Ni; uptake; concentration; maize.

### INTRODUCTION

Nickel is a heavy metal that is not essential for the growth and development of the majority of plant species. Under normal conditions, plants take up small quantities of Ni from soils. However, Ni can be toxic to plants when its concentration in the soil is high. This is the case with severely polluted soils. It is well known that the main sources of Ni and other heavy metals in a soil are the substrate from which the soil was originally formed and anthropogenic pollution. Significant amounts of Ni can be introduced into soils through application of high doses of sewage sludge and certain mineral and organic fertilizers.

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The most common symptom of Ni phytotoxicity is chlorosis, which seems to be Fe-induced. In plants under Ni stress, the absorption of nutrients, root development and metabolism are strongly retarded. Before acute Ni toxicity symptoms are evident, elevated concentrations of this metal in plant tissues are known to inhibit photosynthesis and transpiration.<sup>1</sup> Both plant and pedological factors affect Ni uptake by plants, but the soil pH has the most pronounced influence. As Berrow and Burridge<sup>2</sup> found, increasing the soil pH from 4.5 to 6.5 decreased the Ni content in oat grain by a factor of about 8. Apart from the soil pH, soil organic matter and clay minerals have significant influence on the uptake of Ni by plants.

Agrotechnical measures can change some of the soil properties and, in this way, affect the uptake of Ni and other heavy metals by plants. Liming and addition of organic matter result in a decrease of both the available Ni and the amount taken up by plants.<sup>3</sup> In Serbia, here have not been many studies in which this problem was addressed. Zarković and Blagojević<sup>4</sup> studied the effect of some agrotechnical measures on the uptake of lead (Pb) by maize plants. They found that the application of mineral fertilizers decreased the uptake of Pb by the roots and its transport to the shoots.

The purpose of the present investigation was to determine the effect of fertilization, soil acidification and liming on the uptake of Ni by maize plants grown on some alluvial soils.

#### EXPERIMENTAL

A pot experiment was set up with maize (hybrid ZP 704) that was grown on alluvial soils collected from the following locations in Serbia: Salinac, Velika Plana, Lipe, Osipaonica, Mala Krsna and Kragujevac. Before the experiment was set up, the soil samples were analyzed for the following chemical properties:

- the soil pH in water and 1.0 M KCl (potentiometrically with a glass electrode);
- the humus content (the Tiurin method modified by Simakov);
- the total N content (the Kjeldahl method modified by Bremner);
- the available phosphorus and potassium (the AL-method according to Egner–Riehm);
- total Ni content (atomic absorption spectrophotometry after digestion of the samples with a mixture of nitric, perchloric and hydrofluoric acid).

All the aforementioned methods are described in detail in the *Laboratory Manual in Agrochemistry*.<sup>5</sup>

After determination of the pH, it was decided that the pot experiment would be performed with 4 neutral to weakly alkaline soils (pH in H<sub>2</sub>O from 7.16 to 7.58) and 2 acid soils (pH in H<sub>2</sub>O 5.76 and 6.36).

The following treatments were applied on the neutral and weakly alkaline soils:

1. control (without fertilizers);
2. NPKI (50 mg N/kg, 50 mg P<sub>2</sub>O<sub>5</sub>/kg and 50 mg K<sub>2</sub>O/kg);
3. NPKII (100 mg N/kg, 100 mg P<sub>2</sub>O<sub>5</sub>/kg and 100 mg K<sub>2</sub>O/kg);
4. NPKI (soil acidified to pH 5.5 in 1M KCl);
5. NPKI (soil acidified to pH 4.5 in 1M KCl).

The following treatments were applied on the two acid soils:

1. control (without fertilizers);
2. NPKI (50 mg N/kg, 50 mg P<sub>2</sub>O<sub>5</sub>/kg and 50 mg K<sub>2</sub>O/kg);
3. NPKII (100 mg N/kg, 100 mg P<sub>2</sub>O<sub>5</sub>/kg and 100 mg K<sub>2</sub>O/kg);
4. NPKI + 1/2 of the amount of CaCO<sub>3</sub> required for soil neutralization;
5. NPKI + the amount of CaCO<sub>3</sub> required for soil neutralization.

Nitrogen was added as NH<sub>4</sub>NO<sub>3</sub>, phosphorus as Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O and potassium in the form of KCl. All three nutrients were added as solutions of the aforementioned salts. Soil acidification (to pH 5.5 and 4.5 in 1.0 M KCl) was performed with 5.0 M H<sub>2</sub>SO<sub>4</sub>. Partial and full neutralization of the two acid soils was realized by means of calcium carbonate, the amount of which was calculated on the basis of the value for hydrolytic acidity.

Each experimental treatment was repeated three times. The soil moisture was maintained at 60 % of the water holding capacity during the experiment. The experiment lasted for 6 weeks. At the end of the experiment, the yield of young maize plants was measured. The roots and the aerial part of the maize plants were analyzed for the concentration of Ni by atomic absorption spectrophotometry, which was performed after digestion of the samples with nitric and perchloric acid.<sup>6</sup>

The obtained analytical data were subjected to statistical analysis (analysis of variance and correlation analysis). It is important to mention that the LSD test was performed only in cases where statistical significance of the corresponding *F* values was found.

#### RESULTS AND DISCUSSION

The results of the determination of some chemical properties of the alluvial soils are presented in Table I.

TABLE I. Some important chemical properties of alluvial soils

Soil-location	pH		Humus %	Total N %	Available		Total Ni mg/kg
	H <sub>2</sub> O	nKCl			P (mg P <sub>2</sub> O <sub>5</sub> /100 g)	K (mg K <sub>2</sub> O/100 g)	
1-Salinac	7.42	6.76	2.09	0.134	8.1	21.7	116
2-Velika Plana	7.58	6.70	2.70	0.200	5.2	36.0	148
3-Lipe	7.16	6.27	3.55	0.228	35.0	40.0	115
4-Osipaonica	7.22	6.18	3.25	0.275	17.5	21.6	144,5
5-Mala Krsna	6.36	5.28	3.37	0.216	1.4	22.5	122,5
6-Kragujevac	5.76	4.66	2.49	0.171	4.1	14.9	45

According to the pH values in water, four soils (Lipe, Osipaonica, Salinac and Velika Plana) are neutral to weakly alkaline, while the soils from Mala Krsna and Kragujevac are acid. The content of organic matter in the soils is medium. The obtained values indicate that soils 1, 2, 5 and 6 have low content of available phosphorus, while it is high in soil from Lipe. All soils are well supplied with available potassium. It can be seen from the Table I that the total Ni concentration is in the interval from 45 to 148 mg/kg. The highest value was found in the soil sample from Velika Plana. Maximum allowed Ni concentration in agricultural soils is 50 mg/kg.<sup>7</sup>

The concentration of Ni found in the roots is shown in Tables II and III. Statistical analysis of data (analysis of variance) indicates that the treatment as an

experimental factor had a significant influence on the concentration of Ni in the roots of young maize plants that were grown on neutral and weakly alkaline soils. Namely, the corresponding *F*-values were significant at the 0.01 probability level. The average Ni concentration in the roots ranged from 52.1 to 78.1 µg/g, while corresponding removal of Ni from the soil ranged from 37.1 to 64.1 µg/pot. The highest average value for Ni concentration in plant tissues and its removal from the soil was found with the treatment NPKI (pH 4.5), while the lowest was found with the treatment NPKII. From the results presented in Table II, it can be seen that the higher dose of mineral fertilizers (treatment NPKII) caused a significant decrease in the Ni concentration in the plant roots and its removal from the soil by the roots. It can be assumed that part of the available Ni was transformed into less soluble compounds under the influence of the applied phosphate ions. Soil acidification (to pH 5.5 and 4.5) increased the root Ni concentration and its removal from the soil. This effect was especially pronounced with treatment NPKI (pH 4.5), which can be explained by the considerably higher mobility of Ni at this pH value. It is well known from the literature<sup>8</sup> that the mobility and availability of Ni is higher in acid in relation to neutral and weakly alkaline soils. Ni phytotoxicity occurs when highly contaminated soils are strongly acidic.<sup>9</sup> Soil as an experimental factor also exerted a statistically significant influence on the uptake of Ni by maize roots. Comparison of the average values for the uptake of Ni from the investigated soils indicates that the highest average removal of Ni from the soil was found for soil 3 (70.2 µg/pot), while it was the lowest for soil 1 (42.3 µg/pot). There was no significant difference between soils 3 and 4 with respect to Ni removal from the soil.

TABLE II. Concentration of Ni in the roots and its removal from treated neutral and weakly alkaline soils; results of the LSD test for Ni concentration: treatment – LSD (0.05) = 13.8 and LSD (0.01) = 18.4; results of the LSD test for Ni uptake: treatment – LSD (0.05) = 16.7 and LSD (0.01) = 22.3, soil – LSD (0.05) = 13.6 and LSD (0.01) = 18.2

Treatment	Soil 1		Soil 2		Soil 3		Soil 4		Average value	
	µg/g	µg/pot	µg/g	µg/pot	µg/g	µg/pot	µg/g	µg/pot	µg/g	µg/pot
Control	47.5	31.1	50.5	27.3	75.5	85.2	78	67.4	62.9	52.8
NPKI	73.5	48.1	76.5	62.9	64	66	78	66.9	73.0	61.0
NPKII	46	30.1	48	25.6	45	41.9	69.5	50.9	52.1	37.1
NPKI (pH 5.5)	60	50	54.5	37.8	79	91.5	76	65.2	67.4	61.1
NPKI (pH 4.5)	68.5	52.2	84	62.5	74.5	66.6	85.5	74.9	78.1	64.1
Average	59.1	42.3	62.7	43.2	67.6	70.2	77.4	65.1	66.7	55.2

Only soil as an experimental factor had a statistically significant influence on the concentration of Ni in maize roots and Ni removal by roots from acid soils (Table III). This was determined by statistical analysis. The average values for the Ni concentration in plant roots and Ni removal from the soil were higher for the treatments of soil 5 than of soil 6. This was connected with the fact that soil 5



had a higher concentration of total Ni than soil 6. From the Table III, it can be seen that with treatments NPKI and NPKII, root Ni concentration and Ni removal from the soil were lower than in the control. Full neutralization of the acid soils increased Ni removal from the soil by the roots in relation to all other experimental treatments. However, it must be bear in mind that the registered changes in the root Ni concentration and Ni removal from the soil were not significant at the 0.05 probability level.

TABLE III. Concentration of Ni in the roots and its removal from the treated acid soils; results of the LSD test for Ni concentration: soil – LSD (0.05) = 16.8 and LSD (0.01) = 22.8; results of the LSD test for Ni uptake: soil – LSD (0.05) = 23.2 and LSD (0.01) = 31.5

Treatment	Soil 5		Soil 6		Average value	
	µg/g	µg/pot	µg/g	µg/pot	µg/g	µg/pot
Control	105.0	78.8	53.5	26.0	79.3	52.4
NPKI	74.5	76.9	45.5	19.9	60.0	48.4
NPKII	57.5	55.9	46.0	17.9	51.8	36.9
NPKI + 1/2 CaCO <sub>3</sub>	66.0	57.4	55.5	21.0	60.8	39.2
NPKI + CaCO <sub>3</sub>	102.0	132.8	57.0	32.5	79.5	82.7
Average	81.0	80.4	51.5	23.5	66.3	51.9

The found values for the Ni concentration in the shoots and for the uptake of Ni from treated neutral and weakly alkaline soils are given in Table IV. The average values (according to treatments for all 4 soils) for the Ni concentration in the shoots ranged from 6.8 to 12.0 µg/g, while the corresponding values for Ni removal ranged from 8.8 to 16.7 µg/pot. Analysis of the variance showed that none of the experimental factors had a statistically significant influence on the shoot Ni concentration and its removal from the soil. In other words, the differences in the Ni concentration and its removal (in shoots and by shoots, respectively), which existed between the treatments and the soils were not significant at the 0.05 probability level.

TABLE IV. Concentration of Ni in the shoots and its removal from the treated neutral and weakly alkaline soils

Treatment	Soil 1		Soil 2		Soil 3		Soil 4		Average value	
	µg/g	µg/pot	µg/g	µg/pot	µg/g	µg/pot	µg/g	µg/pot	µg/g	µg/pot
Control	14.0	15.3	11.5	10.4	8.0	15.0	8.5	12.2	10.5	13.2
NPKI	6.0	6.5	6.5	8.9	7.5	12.9	7.0	10.0	6.8	9.6
NPKII	7.0	7.6	7.0	6.2	7.5	11.6	8.0	9.8	7.4	8.8
NPKI (pH 5.5)	6.5	9.0	7.5	8.7	7.0	13.5	6.0	8.6	6.8	10.0
NPKI (pH 4.5)	6.0	7.6	10.0	12.4	8.0	11.9	24.0	35.0	12.0	16.7
Average	7.9	9.2	8.5	9.3	7.6	13.0	10.7	15.1	8.7	11.7

Comparison of the treatments with fertilizers and the control showed that the Ni concentration in the shoots and its removal were lower for soils to which only



mineral fertilizers were applied. Soil acidification to pH 4.5 increased the shoot Ni concentration and Ni removal from the soil in relation to the control and other treatments on neutral and weakly alkaline soils. However, as mentioned earlier, the registered changes were not significant at the 0.05 probability level.

Differences between soils with respect to the total Ni concentration did not have a significant effect on the concentration and transfer of Ni into the maize shoots. The highest average values for the Ni concentration and uptake were found for the treatments of soil 4.

The results presented in Table V indicate that treatment, as an experimental factor, did not have a significant influence on the concentration of Ni in the plants (aerial part) and its transfer to the shoots in the experiment with the acid soils. On the other hand, soil, as an experimental factor, did exert a significant influence on the uptake of this metal. The average value of Ni removal from soil 5 was 13.5 µg/pot, while the corresponding value for soil 6 was 6.4 µg/pot. The reason for this lies in the fact that average maize yield on soil 5 was two times higher than that on soil 6.<sup>10</sup> The highest average value for Ni removal from the soil by maize was found for the treatment NPKI + CaCO<sub>3</sub>. However, this increase, with respect to the other treatments, was not significant at the 0.05 probability level.

TABLE V. Concentration of Ni in the maize shoots and its removal from the treated acid soils; results of the LSD test for Ni uptake: soil – LSD (0.05) = 5.0 and LSD (0.01) = 6.7

Treatment	Soil 5		Soil 6		Average value	
	µg/g	µg/pot	µg/g	µg/pot	µg/g	µg/pot
Control	7.0	8.8	9.0	7.3	8.0	8.1
NPKI	7.5	12.9	9.0	6.6	8.3	9.8
NPKII	6.5	10.5	9.5	6.2	8.0	8.4
NPKI +1/2 CaCO <sub>3</sub>	10.0	14.5	8.5	5.4	9.3	10.0
NPKI + CaCO <sub>3</sub>	9.5	20.6	7.0	6.7	8.3	13.7
Average	8.1	13.5	8.6	6.4	8.4	10.0

The results that are presented in Tables II–V indicate that the concentration of Ni was higher in the roots than in the shoots of maize plants. Thus, for example, the average Ni concentration in the roots of maize plants on neutral and weakly alkaline soils was 66.7 µg/g, while the corresponding value for the shoots was 8.7 µg/g. The results obtained by Radulović<sup>11</sup> also indicated that the concentration of Ni was higher in the roots than in the shoots. These investigations refer to oat plants that were grown under controlled conditions on the brown and alluvial soils of the Zeta Plain in Montenegro. This author found that the ratio between Ni concentration in roots and shoots of oat grown on brown soils was 1:0.12, while the corresponding value on the alluvial soils was 1:0.15. Investigations carried out by Sauerbeck and Hein<sup>12</sup> showed that the concentration of Ni

was the highest in the roots. Namely, they investigated the uptake of Ni by 13 plant species grown on two types of soil containing Ni in different concentrations and forms.

Correlation analysis was employed to investigate the relationship between the Ni concentration (in roots and shoots of maize) and the chemical properties of the investigated soils. For the calculation of correlation coefficients, results referring to all three replications of unfertilized treatment (controls) were used. The results of the correlation analysis are presented in Table VI.

TABLE VI. Correlation coefficients between the Ni concentration in maize and some important chemical properties of soil

Soil property	Correlation coefficient	
	Roots	Shoots
pH (H <sub>2</sub> O)	ns <sup>a</sup>	0.530 <sup>b</sup>
pH (1M KCl)	ns	0.624 <sup>c</sup>
Humus	0.821 <sup>c</sup>	-0.860 <sup>c</sup>
Total N	0.619 <sup>c</sup>	-0.708 <sup>c</sup>
Available phosphorus	ns	ns
Available potassium	ns	ns
Total Ni	ns	ns

<sup>a</sup>Not significant; <sup>b</sup>statistically significant at the 0.05 probability level; <sup>c</sup>statistically significant at the 0.01 probability level

The results presented in Table VI indicate that only the content of humus and total nitrogen had a significant influence on the concentration of Ni in the roots of young maize plants. Therefore, it can be supposed that the Ni present in the roots originated partly from its organic forms in the soil. In other words, the fraction of Ni bound to the organic matter of the soil contributed to the supply of plants with this element.

Concerning the concentration of Ni in the shoots, medium and statistically significant correlations were obtained with pH (in H<sub>2</sub>O and 1 M KCl), the humus content and the total soil nitrogen. It can be seen that an increase in the humus and nitrogen content bring about a decrease in the Ni concentration in maize shoots. A good explanation for the positive effect of soil pH and the negative effect of humus content on the Ni concentration in maize shoots cannot be given at present.

There is a negative and statistically very significant correlation between concentrations of Ni in the roots and shoots ( $r = -0.811$ ).

Multiple linear regression was employed to determine the simultaneous impact of several soil properties on the Ni concentration in maize roots and shoots. The investigated chemical properties were assumed as independent variables for the equation constructed by progressive stepwise regression. The following soil



characteristics were considered in the equation describing the Ni concentration in the roots and the aerial parts of the tested plants:

$$\begin{aligned} \text{Ni}_{\text{roots}} &= -24.712 + 40.477 \text{humus} - 120.956N \\ \text{Ni}_{\text{shoot}} &= 11.226 - 0.660 \text{pH}_{\text{H}_2\text{O}} + 2.207 \text{pH}_{\text{KCl}} - 3.161 \text{humus} - 4.836N \end{aligned}$$

where humus is the humus content in % and N is the total nitrogen content in %.

#### CONCLUSIONS

Based on the results obtained in this investigation, the following conclusions can be drawn:

- The addition of mineral fertilizers (without application of other measures) mainly decreased the Ni concentration in maize and Ni removal from the soil by the plants.
- Soil acidification (to pH 4.5) caused an increase in the Ni concentration in the plants and its removal from the soil.
- Liming of acid soils had a positive effect on the removal of Ni from the soil by young maize plants.
- The concentration of Ni in the roots was on average 8 times higher than in the shoots. The obtained results are important from the standpoint of reducing the pollution of plants with potentially toxic heavy metals.
- Correlation analysis indicated that some of the chemical properties of the investigated soils had a statistically significant influence on the concentration of Ni in the roots and shoots of young maize plants. The strongest effect was expressed by the humus content.

#### ИЗВОД

УТИЦАЈ НЕКИХ АГРОТЕХНИЧКИХ МЕРА НА УСВАЈАЊЕ

НИКЛА БИЉКАМА КУКУРУЗА

БРАНКА ЖАРКОВИЋ И СРЂАН БЛАГОЈЕВИЋ

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Никл није неопходан елемент за исхрану већине биљних врста и он може бити токсичан за биљке када је његова концентрација у земљишту висока. Неколико особина земљишта има утицај на усвајање овог метала биљкама. Циљ овог истраживања је био да се утврди утицај ћубрења, закисељавања земљишта и калцизације на усвајање Ni биљкама кукуруза гајеним на неким алувијалним земљиштима. Постављен је оглед у судовима са биљкама кукуруза које су гајене на поменутим земљиштима. Оглед је трајао 6 недеља. Коренови и надземни делови су анализирани на садржај Ni. Може се закључити из резултата огледа да коренови имају веће концентрације Ni у односу на надземне делове. Додавање минералних ћубрива (без примене других мера) углавном је смањило концентрацију и усвајање Ni кореновима као и његов транспорт до надземних делова. Закисељавање земљишта (до pH 4,5) повећало је усвајање Ni кореновима и његов транспорт до надземних делова биљака. Калцизација киселих земљишта је имала позитиван утицај на усвајање Ni младим биљкама кукуруза. Добијени резултати су значајни за смањење загађивања биљака потенцијално токсичним тешким металима.

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## REFERENCES

1. A. Kabata-Pendias, *Trace elements in soils and plants*, CRC Press, Boca Raton, FL, 2001
2. M. L. Berrow, J. C. Burridge, *Sources and distribution of trace elements in soils and related crops*, CEP Consultants Ltd., Edinburgh, 1979
3. R. L. Halstead, B. J. Finn, A. J. MacLean, *Can. J. Soil Sci.* **49** (1969) 335
4. B. Žarković, S. Blagojević, *J. Environ. Prot. Ecol.* **8** (2007) 535
5. D. Stevanović, R. Džamić, M. Jakovljević, *Practicum in Agrochemistry*, Faculty of Agriculture, Belgrade, 1996
6. J. B. Jones, V. W. Case, in *Soil Testing and Plant Analysis*, R. L. Westerman, Ed., Soil Science Society of America, Madison, WI, 1990, p. 404
7. *Regulations of allowed concentrations of heavy metals and organic matter in soil*, Official Gazette, Official Informatory of the Republic of Serbia, 1990, p. 11
8. W. H. Fuller, in *Movement of selected metals, asbestos and cyanide in soil: application to waste disposal problem*, US-EPA, Cincinnati, OH, 1977, p. 243.
9. G. Siebielec, L. R. Chaney, U. Kukier, *Plant and Soil* **299** (2007) 117
10. B. Žarković, *Ph.D. Thesis*, Faculty of Agriculture, Belgrade, 2005
11. M. Radulović, *Ph.D. Thesis*, Faculty of Agriculture, Belgrade, 2001
12. D. R. Sauerbeck, A. Hein, *Water Air Soil Pollut.* **57–58** (1991) 861.

