

# COMPARISON OF BROWN SOIL OF DIFFERENT EXPOSURES IN THE AREA OF THE NATIONAL PARK "UNA" WITH SPECIAL EMPHASIS ON THE DISTRIBUTION OF CADMIUM, NICKEL AND ARSENIC

ORIGINAL SCIENTIFIC PAPER

Fatima Muhamedagić

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University of Bihac, Biotehnicka fakultet, St. Luke Marjanovica bb, 77000 Bihac, Bosnia and Herzegovina

✉ fatima.muhamedagic@gmail.com

## ABSTRACT:

The paper presented results of a comparison of brown soils of different exposures at two different sites within the National Park „Una“. The sites were related to the southwestern exposure (SW) and the northeastern exposure (NE) of the same land use (orchard). The main objective of the research, in addition to the physical and chemical parameters of soil quality, was to determine the distribution of the total content of cadmium (Cd), nickel (Ni) and arsenic (As). The total content of these elements were observed in composite samples at two depths of 0 – 10 and 0 – 20 cm and horizons profile. Their total content was measured by atomic adsorption spectrometry – AAS. The results were statistically analyzed using Kruskal - Walisovog test at the significance level of  $p \leq 0.05$  using correlation coefficient  $\chi^2$ . The results showed a single legality of the distribution of Cd, Ni and As in samples of soil profile, while the average soil samples showed unique legality of the distribution of observed elements.

**KEYWORDS:** brown soil, distribution, cadmium, nickel, arsenic

## INTRODUCTION

The area of the National Park „Una“ has always aroused the interest of many scientists and researchers [1]-[3]. In particular, the issues of distribution of toxic elements in the soil have been dealt with, both in our country and the world, by many researchers coming from different functional areas: industrial [4]-[6], urban [7], landfills [8] and protected areas [9]-[11]. Especially the problem of deposition of various emissions under the influence of wind as a transmission factor was dealt with [12]-[16] and found that depending on the direction, intensity and frequency of wind can transmit various emissions (dry and wet) over long distances from the source. There is also monitoring of deposition monitoring, for example within the UN organization<sup>1</sup>, within the EEA Agency<sup>2</sup>, etc. In Bosnia and Herzegovina, air quality monitoring is performed at the entity level (F BH, RS and BD).

This paper presents the results of a comparison of brown soil of different exposures of the same land

use (orchard) at an inclination within the NP „Una“. The research was performed with the aim of comparing soil samples from two localities of the same soil type (brown soil, opposite exposures (southwest – SW and northeast – NE), with the same sampling depths of average samples and approximately the same altitudes. The study has placed a special emphasis on the distribution of the total content of cadmium (Cd), nickel (Ni) and arsenic (As) in the average samples (0 – 10 and 0 – 20 cm) and by depth of the soil profile. Selected research sites were located on the slopes of the southwestern (SW) and northeastern (NE) exposures in the Cukovi settlement. The first site SW – southwest exposure (altitude: 400 m, wind speed: 6 m/s, pressure: 1354.56 hPa) and the second locality NE – northeast exposure (altitude: 448 m, wind speed: 11 m/s, pressure: 1388.42 hPa). Both sites have the same land use (orchard). The northeastern locality is otherwise exposed to the prevailing wind gusts (Figure 1).

<sup>1</sup> Monitoring and control data. EANET Monitoring

<https://www.eanet.asia/about/monitoring/>

<sup>2</sup> Global Monitoring for the Environment and Security (GMES) – Atmosphere Services, <https://www.eea.europa.eu/themes/air/links/research-projects/global-monitoring-for-the-environment>



**Figure 1.** Slopes of opposite exposures in the settlement of Čukovi

According to pedological maps of BH [17] and pedological interpreters (Bihac 3), brown soils alternate from deep to very shallow at selected localities. Lighter mechanical composition – sandy loam to sandy clay in the upper layers, and the depth of the soil profile heavier – clay and heavy clay. The soils are porous (P) and have medium and moderate capacities for water ( $K_w$ ) and air ( $K_a$ ). The soils are weakly humus, poor in potassium ( $K_2O$ ) and phosphorus ( $P_2O_5$ ), slightly richer in calcium carbonate ( $CaCO_3$ ). Their color is usually brown and yellow-brown.

## MATERIALS AND METHODS

This paper presents results of the field research, sampling and laboratory testing. All analyzes of soil samples were determined according to standardized methods: Mechanical composition (Modified method B pipettes, ISO 11277); Structure (Method by Sekera); The rights specific gravity, Porosity (Conventional method, ISO 11508); The volume specific gravity (Gravimetric method by Kopecky, ISO 11272); Actual humidity, Capacity of soil for water and Air capacity (Gravimetric method, ISO 11465); Humus (Spectrophotometric method, ISO 10694);  $CaCO_3$  (Volumetric method ISO 10693); pH (Electrometric method, ISO 10390); El.conductivity (Electrometric method, ISO 11265);  $P_2O_5$  and  $K_2O$  (Al method, ISO 19730) and The total content of metals and metalloids in the soil (Extraction  $HCl/HNO_3 = 3:1$ , ISO 11466). A total of two pedological profiles were opened at the sites of research and average samples were taken from two soil depths: 0 – 10 cm and 0 – 20 cm. Preparation of soil samples was carried out at the Biotechnical Faculty of the University of Bihac. All analyses of soil samples were carried out in the laboratory of the

Institute of Soil Science, Agrochemistry and Reclamation of the Faculty of Agricultural and Food Sciences, University of Sarajevo, except for the content of arsenic that was carried out at the Faculty of Agriculture, University of Zagreb, and the Institute for Medical Research and Occupational Health in Zagreb. Statistical analysis was performed by the Kruskal – Wallis test at the level of significance of  $p \leq 0.05$ . To determine the relation and distribution of Cd, Ni and As in the soil we used the correlation coefficient ( $\chi^2$ ) [18], [19]. Data were statistically analyzed using SPSS 17. The maximum allowable amounts of total contents were determined in accordance with the current regulations [20] in relation to the soil texture (MRL) and the use of soil in organic farming (MRL-OF). Used are orthophoto imagery in the scale of 1:5000 and 1:75000, topographic maps and GIS.

## RESULTS AND DISCUSSION

Results of the study on the comparison of brown soils with the same soil use but opposite exposures provide:

*Description of the brown soil profile at the site of the southwestern (SW) exposure (Figure 2)*

Site: the slope of the southwestern exposure – SW (N 44° 39.810', E 16° 04.059')

Vegetation: orchard (plum)

Use: orchard

Parent substrate: limestone

Ah	0-19 cm: surface layer intertwined with roots, yellow-brown in colour, with fine granular structure and sandy loamy clay texture (sand = 47.9 %, powder = 25.2 %, clay = 26.9 %)
A/(B)	19-42 cm: transitional horizon, dark yellow-brown colour with evident sprouted roots and clay loam texture (sand = 38.0 %, powder = 32.1 %, clay = 29.9 %)
(B)	42-68 cm: cambic horizon, no visible plant roots, dark yellow-brown colour with skeleton (20%) and clay loam texture (sand = 31.0 %, powder = 36.0 %, clay = 33.0 %)
(B)	68-100 cm: skeleton (> 30%) with fine granular structure and clay texture (sand = 28.0 %, powder = 33.0 %, clay = 39.0 %).
C	>100 cm: coarse limestone

*Description of the brown soil profile at the site of the northeast (NE) exposure (Figure 3)*

Site: the slope of the northeast exposure – NE (N 44° 39.571', E 16° 03.537')

Vegetation: orchard (plum)

Use: orchard

Parent substrate: limestone

Ah	0-19 cm: surface layer intertwined with roots, dark yellow-brown in colour, with granular structure and sandy clay texture (sand = 62.1 %, powder = 1.1 %, clay = 36.8 %)
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(B)	19-45 cm: adhesive layer with skeleton (> 50%) and clay texture (sand = 27.6 %, powder = 29.1 %, clay = 43.3 %)
C	>45 cm: crumbly coarse limestone



Figure 2 – 3. Profiles of soil at the sites SW (left) and NE (right)

#### Physical properties of soil at the sites of SW and NE

The stability of the structural aggregates in the depth of the profile was very good to good. The mechanical composition in the surface layer was lighter – sandy loamy clay, in deeper layers – clay.

The soils were porous, with medium soil water and moderate soil air capacities.

Mean values of real and bulk specific density also indicated that the soils were porous. Overview of the physical properties of the soil is provided in Table 1.

Table 1. The physical properties of the soil profile ( $\Sigma n = 18$ )

Parameters	$X_{mv} \pm X_{se}$	min	max	V	$\sigma$
S	SW 3.16 ± 0.27	2.00	4.00	0.87	0.93
	NE 1.66 ± 0.33	1.00	3.00	0.66	0.81
$P_{sg}$ (g/cm <sup>3</sup> )	SW 2.61 ± 0.03	2.50	2.76	0.01	0.09
	NE 2.58 ± 0.01	2.56	2.60	0.00	0.01
$V_{sg}$ (g/cm <sup>3</sup> )	SW 1.42 ± 0.03	1.23	1.56	0.01	0.09
	NE 1.27 ± 0.02	1.21	1.33	0.00	0.04
P (%)	SW 46.35 ± 1.00	42.30	50.70	9.15	3.02
	NE 48.96 ± 0.54	48.00	49.90	0.90	0.95
$K_w$ (%)	SW 38.46 ± 1.06	30.80	41.90	10.19	3.19
	NE 41.86 ± 0.24	41.40	42.20	0.17	0.41
$K_a$ (%)	SW 6.81 ± 0.85	3.80	10.70	5.82	2.41
	NE 8.23 ± 0.46	7.40	9.00	0.64	0.80

SW – southwest exposure; NE – northeast exposure;  $X_{mv}$  – mean value,  $X_{se}$  – statistical error, min – minimum value, max – maximum value, V – variance,  $\sigma$  – deviation, n – numer of samples, S – soil structure,  $P_{sg}$  – the rights specific gravity,  $V_{sg}$  – the volume specific gravity, P – porosity,  $K_w$  – capacity of soil for water,  $K_a$  – air capacity

#### Chemical properties of the soil profile and average samples 0 – 20 cm at sites SW and NE

In open profiles the reactions of pH values of SW and NE ranged from slightly acidic to alkaline. In the

surface layer, the contents of  $P_2O_5$ ,  $K_2O$  and humus were low and deteriorated rapidly with the depth. Total content of  $CaCO_3$  was high with a tendency of increase with the profile depth. Mean values of

measured electro-conductivity of the soil were not indicative of soil salinity at the profile.

Results of the observed chemical parameters in samples (0 – 20 cm) had similar characteristics as the

parameters of the soil profile of the surface layer (Table 2 – 3).

**Table 2.** The chemical properties of the soil profile ( $\Sigma n_{SW-NE} = 18$ )

Parameters		$X_{mv} \pm X_{se}$	min	max	V	$\sigma$
pH <sub>H2O</sub>	SW	8.47 ± 0.04	8.19	8.67	0.02	0.14
	NE	7.62 ± 0.26	7.01	8.25	0.43	0.65
pH <sub>KCl</sub>	SW	7.26 ± 0.02	7.13	7.41	0.005	0.07
	NE	6.27 ± 0.32	5.30	6.98	0.62	0.78
EC ( $\mu$ S/cm)	SW	209.03 ± 9.97	160	271	1193.70	34.55
	NE	149.60 ± 26.47	86	222	4204.20	64.84
K <sub>2</sub> O (mg/100g soil)	SW	11.50 ± 1.09	7.20	19.10	14.32	3.78
	NE	9.56 ± 1.38	4.50	13.50	11.47	3.38
P <sub>2</sub> O <sub>5</sub> (mg/100g soil)	SW	2.04 ± 0.22	1.08	3.45	0.58	0.76
	NE	1.63 ± 0.28	0.77	2.63	0.48	0.69
Humus (%)	SW	0.73 ± 0.16	0.34	1.94	0.34	0.58
	NE	1.63 ± 0.29	0.90	2.52	0.52	0.72
CaCO <sub>3</sub> (%)	SW	6.81 ± 0.30	5.13	8.80	1.14	1.07
	NE	3.61 ± 0.03	3.50	3.70	0.01	0.08

SW – brown deep soil on the southwestern exposure; NE – brown shallow soil on the northeast exposure, n – numer of samples,  $X_{mv}$  – mean value,  $X_{se}$  – statistical error, min – minimal value, max – maximum value, V – variance,  $\sigma$  – deviation

**Table 3.** The chemical properties of the average samples 0 – 20 cm ( $\Sigma n_{SW-NE} = 18$ )

Parameters		$X_{mv} \pm X_{se}$	min	max	V	$\sigma$
pH <sub>H2O</sub>	SW	7.74 ± 0.16	7.06	8.23	0.16	0.40
	NE	7.05 ± 0.05	6.91	7.29	0.02	0.14
pH <sub>KCl</sub>	SW	6.79 ± 0.16	6.28	7.19	0.16	0.4
	NE	5.43 ± 0.04	5.30	5.55	0.01	0.11
K <sub>2</sub> O (mg/100g soil)	SW	27.90 ± 3.52	16.50	36.80	74.61	8.63
	NE	12.23 ± 0.89	9.80	14.80	4.75	2.18
P <sub>2</sub> O <sub>5</sub> (mg/100g soil)	SW	3.25 ± 0.64	1.08	4.89	2.51	1.58
	NE	2.50 ± 0.67	1.19	5.72	2.69	1.64
Humus (%)	SW	2,31 ± 0,20	1,73	2,77	0,25	0,50
	NE	2.65 ± 0.25	1.43	3.10	0.39	0.62
CaCO <sub>3</sub> (%)	SW	3.84 ± 0.20	2.93	4.42	0.26	0.51
	NE	2.32 ± 0.24	1.63	2.93	0.37	0.61

SW – southwest exposure; NE – northeast exposure; n – numer of samples;  $X_{mv}$  – mean value;  $X_{se}$  – statistical error; min – minimal value; max – maximum value; V – variance;  $\sigma$  – deviation

*Distribution of the total contents of Cd, Ni and As in average samples*

In average samples at the sites of SW and NE (0 – 10 and 0 – 20 cm), a significant difference ( $p \leq$

0.05) in the total content of Cd, Ni and As was established (Table 4).



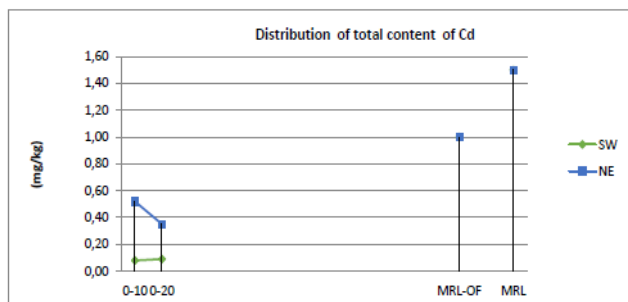
**Table 4.** Distribution of the total contents of Cd, Ni and As in average samples

Observed		$X_{mv} \pm X_{se}$	min	max	V	$\sigma$	$\chi^2$	p
Depth 0 – 10 cm ( $\Sigma n = 9$ )								
Cd (mg/kg)	SW	0.08 ± 0.03	0.08	0.09	0.00	0.05	4.50	p ≤ 0.05
	NE	0.52 ± 0.01	0.52	0.54	0.00	0.01		
Ni (mg/kg)	SW	77.79 ± 0.01	77.80	78.70	0.00	0.01	4.35	p ≤ 0.05
	NE	112.44 ± 0.03	112.40	112.50	0.03	0.05		
As (mg/kg)	SW	9.74 ± 0.03	9.70	9.80	0.03	0.05	3.97	p ≤ 0.05
	NE	17.20 ± 0.00	17.20	17.21	0.00	0.01		
Depth 0 – 20 cm ( $\Sigma n = 9$ )								
Cd (mg/kg)	SW	0.09 ± 0.01	0.08	0.11	0.00	0.01	9.54	p ≤ 0.05
	NE	0.35 ± 0.07	0.17	0.54	0.03	0.19		
Ni (mg/kg)	SW	82.84 ± 2.05	77.80	88.00	30.59	5.53	8.45	p ≤ 0.05
	NE	119.56 ± 2.90	112.40	126.70	60.83	7.79		
As (mg/kg)	SW	10.87 ± 0.50	9.70	12.10	1.53	1.23	8.45	p ≤ 0.05
	NE	18.35 ± 0.48	17.20	19.50	1.57	1.25		

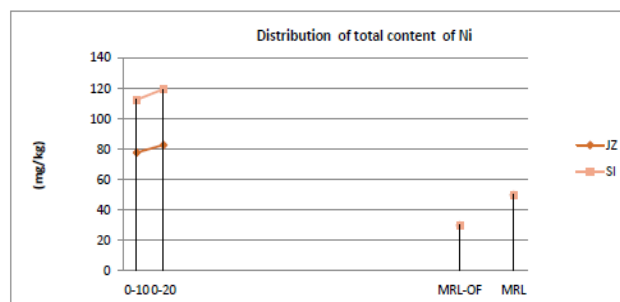
SW – southwest exposure; NE – northeast exposure; n – numer of samples,  $X_{mv}$  – mean value,  $X_{se}$  – statistical error, min – minimal value, max – maximum value, V – variance,  $\sigma$  – deviation,  $\chi^2$  – Kruskal – Wallis coefficient; p – level of significance

In the average samples at the sites of SW and NE (0 – 10 and 0 – 20 cm), total mean contents of Cd and As were lower than the permitted levels of MRL and MRL-OF, while the content of Ni was exceeded MRL and MRL-OF. At the sites SW and NE in depth 0 – 10 cm ( $Cd_{SW} = 0.08$  mg/kg;  $Cd_{NE} = 0.52$  mg/kg;  $Ni_{SW} = 77.79$  mg/kg;  $Ni_{NE} = 112.44$  mg/kg;  $As_{SW} = 9.74$  mg/kg;  $As_{NE} = 17.20$  mg/kg), and the sites SW and NE in depth 0 – 20 cm ( $Cd_{SW} = 0.09$ ;  $Cd_{NE} = 0.35$ ;  $Ni_{SW} = 82.84$  mg/kg;  $Ni_{NE} = 119.56$  mg/kg;  $As_{SW} = 10.87$  mg/kg;  $As_{NE} = 18.35$  mg/kg).

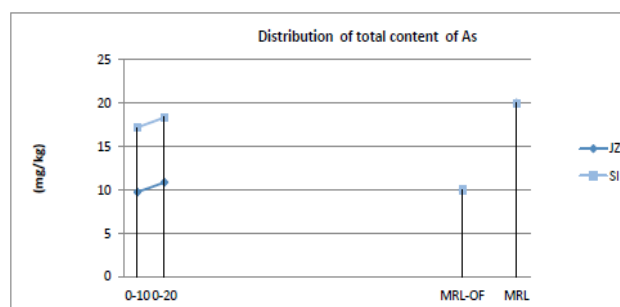
Generally the total contents of the analyzed elements at NE exposure (under the influence of stronger wind gusts) were higher compared to the opposite SW exposure (weaker wind gusts), which confirms the fact of possible atmospheric deposition of dry or wet emissions on wind-affected slopes (Figure 1 – 3).



**Figure 1.** Distribution of the total content of Cd (0 – 10 and 0 – 20 cm)



**Figure 2.** Distribution of the total content of Ni (0 – 10 and 0 – 20 cm)



**Figure 3.** Distribution of the total content of As (0 – 10 and 0 – 20 cm)

*Distribution of the total content of Cd, Ni and As in the soil profiles*

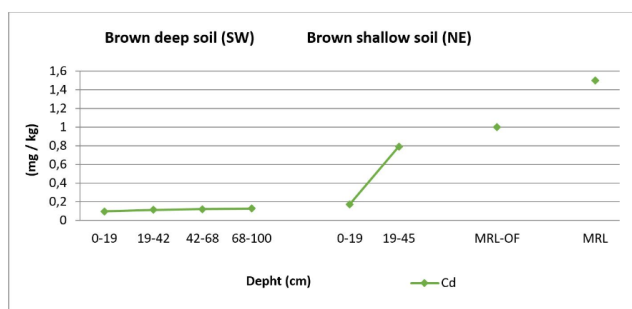
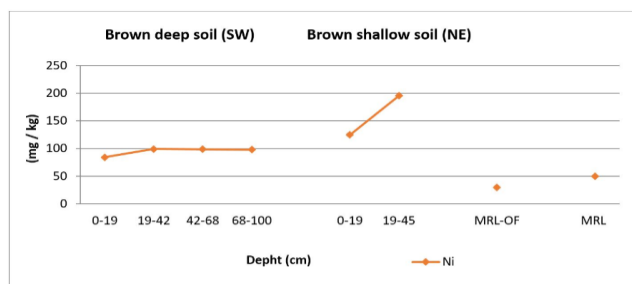
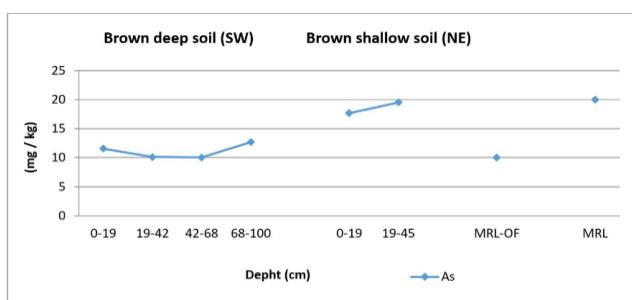
Results of the analysed profiles SW and NE sites of the same use (orchard – plum) have shown significant differences ( $p \leq 0.05$ ) in concentrations of Cd, Ni and As (Table 5).

**Table 5.** Distribution of the total content of Cd, Ni and As in the soil profiles ( $\sum n_{JZ-SI} = 18$ )

Observed		$X_{mv} \pm X_{se}$	min	max	V	$\sigma$	$\chi^2$	p
Cd (mg/kg)	SW	$0.11 \pm 0.00$	0.10	0.13	0.00	0.01	11.37	$p \leq 0.05$
	NE	$0.48 \pm 0.13$	0.15	0.80	0.10	0.33		
Ni (mg/kg)	SW	$95.00 \pm 1.87$	83.66	99.20	42.34	6.50	11.38	$p \leq 0.05$
	NE	$160.01 \pm 15.84$	124.40	195.54	1506.81	38.81		
As (mg/kg)	SW	$11.10 \pm 0.32$	10.00	12.70	1.28	1.13	11.47	$p \leq 0.05$
	NE	$18.60 \pm 0.42$	17.50	19.80	1.08	1.04		

SW – southwest exposure; NE – northeast exposure; n – number of samples;  $X_{mv}$  – mean value,  $X_{se}$  – statistical error, min – minimal value, max – maximum value, V – variance,  $\sigma$  – deviation,  $\chi^2$  – Kruskal – Wallis coefficient; p – level of significance

Observed in general in the examined profiles at the SW and NE sites, the total mean contents of Cd, Ni and AS in the SW exposure profile were higher in relation to the opposite NE (Figure 4 – 6). In the examined profiles, the total mean Cd content on the SW exposure was higher by 78%, for Ni and As by 41% in relation to the opposite NE exposure.

**Figure 4.** Distribution of the total content of Cd in soil profiles**Figure 5.** Distribution of the total content of Ni in soil profiles**Figure 6.** Distribution of the total content of As in soil profiles

## CONCLUSION

At the sites of SW and NE, according to the physical and chemical parameters of soil, stability of structural aggregates declines from good to very good; mechanical composition of the soil in the surface layer – sandy loamy clay, and in the deeper ones – clay. The soils were porous, with medium soil water and moderate soil air capacities.

In general, the pH values at the sites of SW and NE ranged from weakly acidic to alkaline with an upward trend with the profile depth ( $pH_{SW \text{ in } H_2O}$  8.19 – 8.67;  $pH_{SW \text{ in } KCl}$  7.13 – 7.41;  $pH_{NE \text{ in } H_2O}$  7.01 – 8.25;  $pH_{NE \text{ in } KCl}$  5.30 – 6.98) and average samples ( $pH_{SW \text{ in } H_2O}$  7.06 – 8.23;  $pH_{SW \text{ in } KCl}$  6.28 – 7.19;  $pH_{NE \text{ in } H_2O}$  6.91 – 7.28;  $pH_{NE \text{ in } KCl}$  5.30 – 6.55).

In the average samples (0 – 10 and 0 – 20 cm) at the sites, total mean content of Cd were lower than the permitted levels of MRL-OF and MRL ( $Cd_{SW} = 0.08 - 0.11$  mg/kg;  $Cd_{NE} = 0.17 - 0.54$  mg/kg), while the contents of Ni nad As was exceeded MRL-OF and MRL ( $Ni_{SW} = 77.80 - 88.00$  mg/kg;  $Ni_{NE} = 112.40 - 126.70$  mg/kg;  $As_{SW} = 9.70 - 12.10$  mg/kg;  $As_{NE} = 17.20 - 19.50$  mg/kg). In the surface layer, contents of  $P_2O_5$ ,  $K_2O$  and humus were low and decreased with the depth of soil. Calcium carbonate content tended to increase slightly in depth ( $CaCO_{3SW}$  5.13 – 8.80 %;  $CaCO_{3NE}$  3.50 – 3.70 %). The measured levels of soil electrical conductivity were not indicative of the soil salinity ( $EC_{SW}$  160 – 271  $\mu S/cm$ ;  $EC_{NE}$  86 – 222  $\mu S/cm$ ).

In the distribution of Cd, Ni and As in average samples from the sites of exposure SW and NE (0 – 10 and 0 – 20 cm), it was found that there is a significant difference ( $p \leq 0.05$ ) in the total content of Cd, Ni and As.

In general, in the average samples (0 – 10 and 0 – 20 cm) there was a unique tendency of distribution (increase) of the total content of Cd, Ni and As on the NE exposure in relation to the opposite SW exposure. This confirms the fact that atmospheric deposits are deposited on the slopes of exposures that are under

the blows of the dominant wind. In the profiles at the sites (SW and NE), significant differences ( $p \leq 0.05$ ) were determined in the total content of Cd, Ni and As. At the sites of opposite exposures SW and NE, it was determined that the total mean content of Cd, Ni and As in the profiles at NE exposure was higher in relation to the opposite SW, with Cd by 78%, and with Ni and As by 41%.

In this study in the area of the National Park „Una“, in relation to the direction, intensity, dominance (frequency) of the wind, it was found that the total content of Cd, Ni and As at the impact NE exposure was higher. This confirms the fact of deposition in the soil that takes place with the help of wind as a transfer factor.

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