COMPARISON OF ALLUVIAL SOILS OF DIFFERENT LAND USE IN THE AREA OF THE NATIONAL PARK "UNA" WITH SPECIAL EMPHASIS ON THE DISTRIBUTION OF CADMIUM, NICKEL AND ARSENIC

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ABSTRACT

The paper presented results of a comparison of alluvial soils of different land use at two sites within the National Park "Una". The sites were related to a natural meadow (BUK) and artificial meadow (KLISA). 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 cm and 0-20 cm and horizons profile. Their total content was measured by atomic AAS. The results were analyzed using Kruskal – Wallis test (p≤0.05) using coefficient χ^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: *alluvial soil, distribution, cadmium, nickel, aresenic*

INTRODUCTION

In recent decades the area of the National park „Una" has stirred the interest of many scientists and researchers (Alibabić and Bašić, 2005; Bašić and Čustović, 2005; Muhamedagić, 2010, etc). 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 (Shakeri *et al*., 2009; Dheeba and Sampathkumar, 2012, etc.), urban (Romić and Romić, 2003, etc.), landfills (Dellantonio *et al*., 2007, etc.) and protected areas (Maksimović *et al*., 2013; Muhamedagić, 2015, etc.).

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This paper presents the results of a comparison of alluvial soils of different use with in the National Park „Una". 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 in the extensions of alluvial plains along the river Una. The first site of BUK (altitude: 284 m) and the second site of KLISA (altitude: 301 m) (Figure 1-2).

Figure 1 – 2. The sites of soil sampling BUK (left) and KLISA (right)

MATERIAL 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 (ISO 11277); Structure (Method by Sekera); The rights specific gravity, Porosity (ISO 11508); The volume specific gravity (ISO 11272); Actual humidity, Capacity of soil for water and Air capacity (ISO 11465); Humus (ISO 10694); $CaCO_3$ (ISO 10693); pH (ISO 10390); El. conductivity (ISO 11265); P_2O_5 and K_2O (ISO 19730) and The total content of metals and metalloids in the soil (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 Bihać. 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 (χ^2) (Kruskal and Wallis, 1952). Data were statistically analyzed using SPSS 17. The maximum allowable amounts of total contents were determined in accordance with the current

regulations (Official Gazette of the Federation of B&H, No. 72/90) 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 alluvial soils with different use provide:

Description of the alluvial soil profile at the site of BUK (Figure 3)
- Site: alluvial plain – BUK (N 44° 39.042′, E 16° 01.938′);
- Vegetation: meadow;
- Use: natural meadow no cultivation;
- Parent substrate: alluvium

I 0-11 cm: surface layer intertwined with roots, brown in colour, with fine granular structure and sandy loam texture (sand = 68.8%, powder = 16.5%, clay = 14.7%).

II 11-51 cm: abrupt transition to a yellowish-brown layer with evident penetration of roots, with fine granular structure and sandy loam texture (sand=69.0%, powder=15.2%, clay=15.8%).

III 51-110 cm: gradual transition to a greyish-brown layer, with very fine granular structure and sandy clayey loam texture (sand=59.8%, powder = 21.0%, clay=19.2%).

IV > 110 cm: emergence of groundwater.

Description of the alluvial soil profile at the site of KLISA (Figure 4)
- Site: alluvial plain – KLISA (N 44° 35.115′, E 16° 04.487′)
- Vegetation: meadow;
- Use: artificial meadow – cultivated;
- Parent substrate: alluvium.

I 0-24 cm: surface layer is less overgrown with meadow vegetation with shallow root system, brown in colour, with fine granular structure and sandy loam texture (sand = 65.4%, powder = 18.7%, clay = 15.9%).

II 24-82 cm: this layer shows evident traces of rotten plant parts, its structure is finely granular, colour is yellowish brown, and texture sandy loam (sand = 56.9%, powder = 22.5%, clay = 20.6%).

III 82-115 cm: abrupt transition to a layer of grayish-brown colour with evident traces of rotten plants, fine granular structure and sandy clayey loam texture (sand = 55.2%, powder = 23.0%, clay = 21.8%).

IV > 115 cm: emergence of groundwater.

Figure 3 – 4.   Profiles of soil at the sites BUK (left) and KLISA (right)

Physical properties of soil

The stability of structural aggregates in the depth of the profile was very good, good to unstable. Mechanical composition in the surface layer was lighter– sandy loams, and heavier in deeper layers – sandy clayey loams. The soils were porous (KLISA: 51.48 ± 0.42; BUK: 47.51 ± 0.91), with medium soil water (KLISA: 42.36 ± 0.70; BUK: 38.72 ± 0.52) and moderate soil air capacities (KLISA: 9.14 ± 0.44; BUK: 8.57 ± 1.01).

Chemical properties of average samples of soil 0-20 cm

In average samples the reactions of pH values of BUK and KLISA ranged from slightly to very alkaline with an upward trend with the profile depth. 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) are shown in Table 1.

Table 1. The chemical properties in average samples ($\Sigma n = 3$)

Parameters		$X_{mv} \pm X_{se}$	min	max	V	σ
pH in H$_2$O	BUK	8.27 ± 0,03	8.14	8.35	0.01	0.07
	KLISA	8.35 ± 0,04	8.20	8.47	0.01	0.09
pH in KCl	BUK	7.43 ± 0,02	7.35	7.51	0.00	0.05
	KLISA	7.46 ± 0,01	7.42	7.50	0.00	0.02
K$_2$0 (mg/100g tla)	BUK	9.83 ± 1,41	6.20	14.50	12.05	3.47
	KLISA	7.25 ± 0,28	6.50	8.20	0.46	0.68
P$_2$O$_5$ (mg/100g tla)	BUK	4.82 ± 0,41	3.76	6.03	1.10	1.00
	KLISA	5.63 ± 0,20	5.00	6.34	0.24	0.49
Humus (%)	BUK	2.33 ± 0,29	1.64	3.04	0.50	0.71
	KLISA	1.54 ± 0,01	1.53	1.57	0.00	0.01
CaCO$_3$ (%)	BUK	62.79 ± 0,77	60.84	65.97	3.58	1.89
	KLISA	33.35 ± 0,49	31.52	35.18	1.44	1.20

Designation: „BUK" – natural meadow, „KLISA" – artificial meadow, n – number of samples,
X_{mv} – mean value, X_{se} – statistical error, min – minimal value, max – maximum value,
V – variance, σ – deviation

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

In average samples at the sites of BUK and KLISA (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 2).

Table 2. Distribution of the total contents of Cd, Ni and As in average samples

Observed		$X_{mv} \pm X_{se}$	min	max	V	Σ	χ^2	p
Depth0 – 10 cm ($\Sigma n = 3$)								
Cd (mg/kg)	BUK	0.70± 0.01	0.69	0.71	0.00	0.01		
	KLISA	0.94 ± 0.00	0.94	0.95	0.00	0.01	3.95	p ≤ 0.05
Ni (mg/kg)	BUK	39.54 ± 0.01	39.52	39.55	0.00	0.01		
	KLISA	36.01 ± 0.02	35.99	36.05	0.00	0.03	3.97	p ≤ 0.05
As (mg/kg)	BUK	4.40 ± 0.01	4.39	4.42	0.00	0.01		
	KLISA	5.89 ± 0.00	5.89	5.90	0.00	0.01	3.97	p ≤ 0.05

Observed		$X_{mv} \pm X_{se}$	min	max	V	Σ	χ^2	p
Depth 0 – 20 cm (Σn = 3)								
Cd (mg/kg)	BUK	0.52 ± 0.07	0.33	0.71	0.03	0.18		
	KLISA	0.95 ± 0.00	0.94	0.96	0.00	0.01	3.95	$p \leq 0.05$
Ni (mg/kg)	BUK	34.87 ± 1.90	30.20	39.55	26.13	5.11		
	KLISA	39.33 ± 1.35	35.99	42.66	13.22	3.63	2.09	$p \leq 0.05$
As (mg/kg)	BUK	4.30 ± 0.04	4.20	4.42	0.01	0.11		
	KLISA	6.15 ± 0.11	5.89	6.41	0.07	0.27	8.48	$p \leq 0.05$

Designation: „BUK" – natural meadow, „KLISA" – artificial meadow, n – number of samples, X_{mv} – mean value, X_{se} – statistical error, min – minimal value, max – maximum value, V – variance, σ – deviation, χ^2 – Kruskal – Wallis coefficient; p – level of significance

In the average samples at the sites of BUK and KLISA (0-10 cm), total mean contents of Cd and As were lower than the permitted levels of MRL-OF and MRL (Cd_{BUK} = 0.70 mg/kg; Cd_{KLISA} = 0.94 mg/kg; As_{BUK} = 4.40 mg/kg; As_{KLISA} = 5.89 mg/kg), while the content of Ni was bordered MRL and exceeded MRL-OF (Ni_{BUK} = 39.54 mg/kg; Ni_{KLISA} = 36.01 mg/kg). In the samples from the site of BUK (0-20 cm), total mean contents of Cd and As were below the level of MRL-OF and MRL (Cd_{BUK} = 0.52 mg/kg; As_{BUK} = 4.30 mg/kg), while Ni had a tendency of slight decrease compared to the average samples 0-10 cm (Ni_{BUK} 39.54 to 34.87 mg/kg). In the samples from the site of KLISA (0-20 cm), total content of Cd remained the same (0.95 mg/kg) while the contents of Ni and As were slightly increased compared to the average samples 0-10 cm (Ni_{KLISA} 36.01 to 39.33 mg/kg; As_{KLISA} 5.89 to 6.15 mg/kg). Given that these alluvial plains were formed by deposition of allochthonous matter from the surrounding areas and affected by frequent, it is generally difficult to define a single tendency of increase or decrease of total content of Cd, Ni and As in the analyzed average samples (Figure 5 – 7).
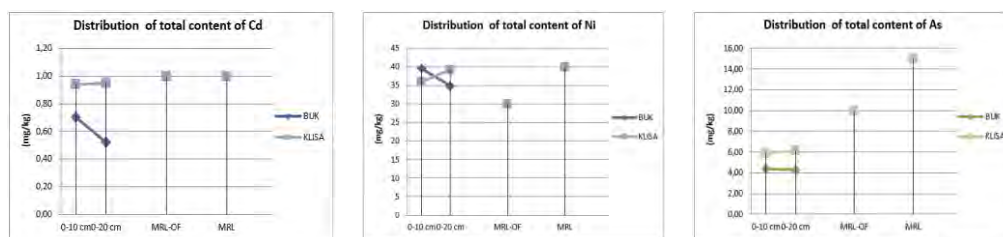

Figure 5 – 7. Distribution of the total content of Cd, Ni and As in average samples

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

Results of the analysed profiles at BUK and KLISA sites of different use (natural and artificial meadow) have shown significant differences ($p \leq 0.05$) in concentrations of Ni and As, and no differences ($p > 0.05$) in Cd (Table 5).

Table 5. Distribution of the total content of Cd, Ni i As in the soil profiles

Observed		$X_{sr} \pm X_{sg}$	min	max	V	σ	χ^2	p
($\Sigma n_{BUK-KLISA}$ = 18)								
Cd (mg/kg)	BUK	0.32 ± 0.13	<0.01	0.96	0.17	0.41	0.88	$p > 0.05$
	KLISA	0.41 ± 0.08	0.17	0.74	0.05	0.24		
Ni (mg/kg)	BUK	48.87 ± 1.00	44.86	51.12	9.02	3.00	7.76	$p \leq 0.05$
	KLISA	41.16 ± 1.99	34.60	48.44	35.99	5.99		
As (mg/kg)	BUK	4.94 ± 0.14	4.38	5.40	0.18	0.43	3.96	$p \leq 0.05$
	KLISA	5.41 ± 0.19	4.69	6.10	0.34	0.58		

Designation: „BUK" – natural meadow; „KLISA" – artificial meadow, n – number of samples, X_{mv} – mean value, X_{se} – statistical error, min – minimal value, max – maximum value, V – variance, σ – deviation, χ^2 – Kruskal – Wallis coefficient; p – level of significance

In the studied profiles at the sites of BUK and KLISA, the total mean contents had a downward trend (Cd_{BUK} 0.96 to < 0.01 mg/kg, Cd_{KLISA} 0.74 to 0.17 mg/kg, Ni_{BUK} 51.12 to 44.86 mg/kg, Ni_{KLISA} 48.44 to 34.60 mg/kg, As_{BUK} 5.40 to 4.38 mg/kg, As_{KLISA} 6.10 to 4.69 mg/kg). In both profiles of the alluvial soil of different use a single tendency of decline of total contents with the increase in depth, i.e. from the surface to the bottom of the profile, was observed in all three analysed elements (Figure 8 – 10).
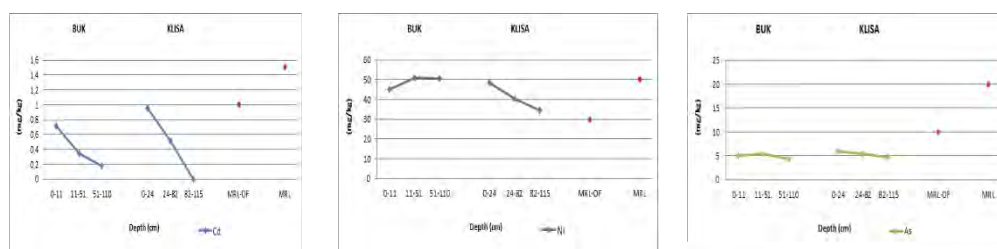

Figure 8 – 10. Distribution of the total content of Cd, Ni and As in soil profiles

CONCLUSIONS

At the sites of BUK and KLISA, according to the physical and chemical parameters of soil, stability of structural aggregates declines from very good to unstable; mechanical composition of the soil in the surface layer – sandy loams, and in the deeper ones – sandy clay loam. The soils are porous and with medium water and moderate air capacity. In the average samples at the sites (0-10 cm and 0-20 cm), total mean contents of Cd and As were lower than the permitted levels of MRL-OF and MRL (Cd_{BUK} = 0.70 mg/kg; Cd_{KLISA} = 0.94 mg/kg; As_{BUK} = 4.40 mg/kg; As_{KLISA} = 5.89 mg/kg), while the content of Ni was bordered MRL and exceeded MRL-OF (Ni_{KLISA} = 36.01 mg/kg; Ni_{BUK} = 39.54 mg/kg). In general, the pH levels established at the sites of BUK and KLISA ranged from slightly to very alkaline with an upward trend with the profile depth ($pH_{BUK\ in\ H20}$ 8.09 to 8.45; $pH_{BUK\ in\ KCl}$ 8.18 to 8.52; $pH_{KLISA\ in\ H20}$ 7.35 to 7.56; $pH_{KLISA\ in\ KCl}$ 7.42 to 7.60). In the surface layer, contents of P_2O_5, K_2O and humus were low and decreased with the depth of soil. The content of calcium carbonate was high with a tendency to increase with depth ($CaCO_{3BUK}$ 31.52 to 65.97%; $CaCO_{3KLISA}$ 20.52 to 41.78%). The measured levels of soil electrical conductivity were not indicative of the soil salinity. In the distribution of Cd, Ni and As in the average samples taken from the sites of BUK and KLISA a significant difference ($p \leq 0.05$) was established in the total content of Cd, Ni and As. Generally, in average samples it was difficult to define a single tendency of distribution (increase or decrease) of the total content of Cd, Ni and As. In the profiles at the sites (BUK and KLISA), significant differences ($p \leq 0.05$) were determined in the total content of Ni and As, and no significant difference ($p > 0.05$) for Cd. Generally, for the sites of BUK and KLISA it was established that the distribution of the content of Cd, Ni and AS in the profiles decreased in relation to the depth (Cd_{BUK} 0.96 to < 0.01 mg/kg; Cd_{KLISA} 0.74 to 0.17 mg/kg; Ni_{BUK} 51.12 to 44.86 mg/kg; Ni_{KLISA} 48.44 to 34.60 mg/kg; As_{BUK} 5.40 to 4.38 mg/kg; As_{KLISA} 6.10 to 4.69 mg/kg).

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