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SPATIAL DISTRIBUTION OF HEAVY METALS AND ASSESSMENT OF THEIR BIOAVAILABILITY IN AGRICULTURAL SOILS OF KOSOVO

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Abstract: From topsoil, 127 samples were collected in agricultural areas of Kosovo, which were analyzed for heavy metals (HM), by extraction with aqua-regia (pseudototal concentration), NH_4OAc-EDTA (potential bioavailable) and NH_4NO_3 (mobile fraction). 62 % of the soil samples showed elevated Ni concentrations, whereas increased values for Pb, Cd, Zn and Cr were in 9 %, 6 %, 5 %, and 2 % of the sample set, respectively. Cu was below threshold values in all analyzed samples. In order to assess the bioavailability of heavy metals, relevant soil parameters were determined. Regarding mobile fractions of HM, only Ni was significantly influenced by its total concentrations. For most of HM in mobile fractions, soil pH significantly impacted the extracted metal amounts. On some field sites crop production may be under risk due to elevated metal concentrations in not only the pseudototal but also in the potentially bioavailable and mobile fractions.

Keywords: pseudototal concentrations, assessment of bioavailable fraction, mobile fraction

1. INTRODUCTION

Mineral dispersion and human activity are two main sources impacting the soil-plant system with heavy metals. Campbell et al., (1983) compared the emitted amounts of heavy metals in the atmosphere, and found that 15 times higher Cd, 100 times higher Pb, 13 times higher Cu, and 21 times higher Zn is emitted from human activity than from natural processes. Thence, soil contamination by heavy elements represents a worldwide environmental concern over decades. These elements can be transferred to the hydrosphere and biosphere, thereby posing a hazard to human health. Consequently, the mobility and bioavailability of heavy elements in soil play an important role in the uptake of these contaminants by vegetation and animals (Nanoni et al., 2011). Total concentrations of trace metals in soil are poor indicators for their bioavailability, yet they are commonly used for the determination of maximum permissible levels in the legislation of many countries. It is of great importance to estimate the total contents of toxic elements and their speciation in soils (Chakroun et al., 2013). Water soluble and exchangeable forms of heavy metals are considered readily mobile and available to plants. Several authors have examined the controlling parameters influencing metal solubility in soils and expressed the correlations by regression models (Ivezić et al., 2012; Gandois et al., 2010; Groenenberg et al., 2010). Such regression models usually include total concentration of trace metals (M (tot)), soil pH, soil organic matter (SOM) and clay content. With increasing pH, content of organic matter, and clay the bioavailability of most metals decreases due to their increased adsorption (Takac et al., 2009).

Several reagents (e.g., $CaCl_2$, NH_4OAc, NH_4NO_3, complexing agents) have been used to extract the ”mobile” or “bioavailable” forms of heavy metals with single extraction procedures (Narwal et al., 1999; He & Singh 1995, Damian et al., 2008). Single extractions provide information on potential mobility as well as bioavailability and plant uptake of heavy metals (Singh 1997).

Several studies showed that the mining

discharges, including the ore processing industry, represent a potential source of contamination for soil (Ditoiu & Osean 2007, Lăcătușu et al., 2009, Galfati et al., 2011, Chakroun et al., 2013). The main heavy metal source contaminating the environment and agricultural soils in Kosovo is the industry, which is mostly located in the eastern part of the country. The following heavy industry sites are found in this area: the ore-metallurgic combine "Trepça" in Mitrovica, the Kosovo Energetic Corporation in Obiliq, "Ferronikeli" in Drenas, the Battery Factory Ni-Cd "IBG-Gjilan", „Cementorja" Hani i Elezit. Many authors report high levels of heavy metals in agricultural soils which are located near these contamination sources, and which surpass many times the permitted values for soils (Nanoni et al., 2011; Maxhuni et al., 2011; Borgna et al., 2009; Elezi & Jusufi 1996). Nevertheless, up to now, there are no accurate data in Kosovo about the level of heavy metals in agricultural soils and contaminated surface soils. Therefore, the aim of this paper is to determine the total level of heavy metals in agricultural soils of Kosovo, to assess the bioavailability of the metals, and to assess the influence of pH and organic matter on their potential for plant uptake.

2. MATERIALS AND METHODS

2.1. Study area

The study area represents agricultural soils in different regions of Kosovo. The Kosovo is a country (10.877 km²) in the center of the Balkan Peninsula (N 43° 16' – 41° 53' and E 21° 16 – 19° 59'). The entire region is divided into three zones developed in the Oligo-Miocene (Gashi & 2002): (i) two plains, the Dukagjini plain in the western, and the Kosovo plain in the eastern part, and (ii) adjacent hilly areas divided by rivers mainly originating in the (iii) surrounding mountain areas. The elevation ranges from 265 m to 2656 m above sea level, with about 80 % of the entire area below 1.000 m. The climate in Kosovo is Continental with Mediterranean influence in the west, with warm summers and cold winters. Air temperatures range from –20°C to +35°C. The main annual rainfall is about 650 mm, and about 170-200 days per year are frost-free. In the western part of Kosovo the climate is more moist (annual rainfall: about 800 mm) and warmer (196-225 frost-free days) than in the eastern part (Mehmeti et al., 2009, 2010; Elezaj & Kodra 2008).

According to a digital map of soil types (scale 1:50000) provided by the Chairman of Soil Sciences of Prishtina University (Elezi et al., 2004) and referring to the WRB-soil classification (IUSS Working Group WRB 2006), more than 80 % of agricultural soil are cambisols, vertisols, fluvisols, regosols and gleysols.

2.2. Soil Sampling

In total, 127 topsoil samples (0-30 cm depth in arable land and 0-5 cm in meadow) were collected throughout the agricultural area of Kosovo (Fig. 1). Each soil sampling has been prepared out of 5 sub samples that have been taken with a distance of 10-50 m between them using a hand auger.

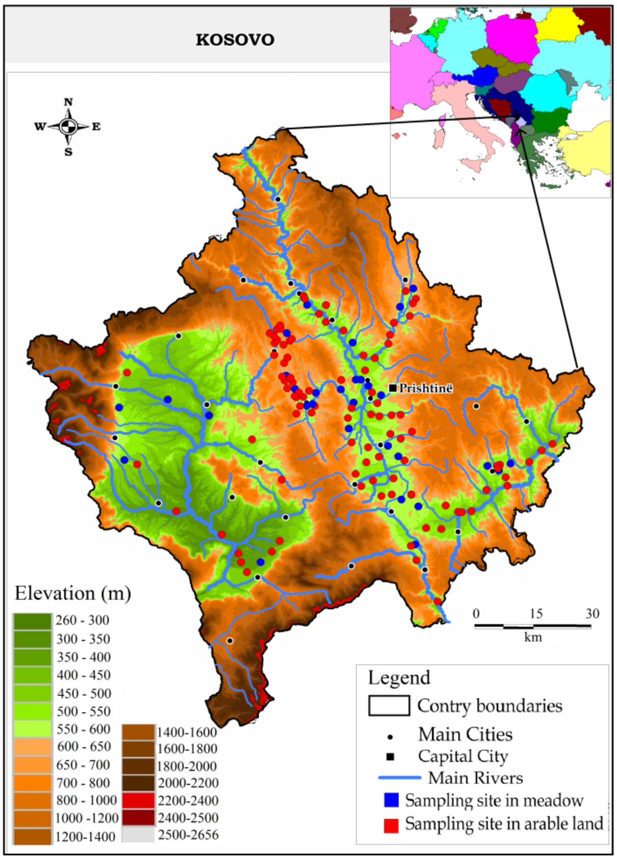


Figure 1. Soil sampling sites in the study area.

The topsoil samples were collected according to the random method (Bundes Bodenschutz und Altlastenverordnung (BbodSchV) 1999; Manual 2006; Theocharopoulos et al., 2011 a, b). A larger number of samples per surface unit has been taken near the contamination sources (smelting, mining, power plant, etc.), whereas a smaller number has been taken from areas that are further remote from those sources. For quality assurance and to prove representativeness of soil sampling, we took 8 samples that have been analyzed individually (8x5=40), and composite samples containing 5 sub samples.

Table 1. Correlation of heavy metal concentrations (mg kg^{-1}) from composite soil sampling and single soil sampling (average)

No	Cd		Cr		Cu		Ni		Pb		Zn	
	CSS	**ASS**	**CSS**	**ASS**	**CSS**	**ASS**	**CSS**	**ASS**	**CSS**	**ASS**	**CSS**	**ASS**
1	0.266	0.282	251.66	246.30	71.67	71.03	415.90	420.72	33.24	32.65	99.85	99.80
2	0.056	0.044	52.08	60.47	21.99	23.20	33.01	36.49	30.84	31.95	39.72	42.14
3	0.113	0.095	201.77	199.95	39.11	37.95	236.08	226.98	28.13	27.26	87.61	85.42
4	0.204	0.228	124.70	122.36	35.09	32.99	155.82	155.35	71.19	71.34	101.09	99.74
5	0.346	0.322	126.81	128.07	31.91	29.90	99.14	92.31	142.58	135.61	91.76	91.92
6	0.109	0.112	89.17	87.86	29.98	35.54	172.07	170.91	43.42	42.22	84.75	84.24
7	0.145	0.132	142.20	139.41	38.63	36.32	164.90	164.08	43.68	42.76	94.20	94.05
8	1.293	1.357	204.20	190.65	69.70	69.06	236.98	251.78	1183.75	1215.71	436.68	458.01
R^2	**0.99**		**0.99**		**0.98**		**0.99**		**0.99**		**0.99**	

CSS-composite soil sampling, SSS- single soil sampling (average)

We could show that there is no significant difference between sub samples, but a very high correlation between the composite samples and the average of sub samples has been revealed (Table 1). A similar correlation between the average of sub samples and the composite ones, has also been reported by Zgorelec et al., (2011).

2.3. Sample analysis

Soil samples were dried at room temperature, sieved for 2 mm, partially finely ground, and stored at room temperature until analysis. Soil pH was measured in H_2O suspension of soil and 0.01M $CaCl_2$ with a ratio of 1:2.5 (DIN ISO 10390 2005). The total amount of organic matter (OM) was determined by the ignition method.

The pseudo-total contents of heavy metals in soil were extracted with aqua regia (3 parts of 35% HCl and 1 part of 65% HNO_3) from finely ground samples (DIN 11466 1995). The term pseudo-total stands for the extraction with aqua regia, which does not completely destroy silicates. As this pseudo-total content is insufficient to determine ecotoxicologically relevant heavy metals, the exchangeable and mobile fractions of heavy metals (potentially plant available and easily leachable), were also extracted with NH_4OAc-EDTA – extract (Ammonium acetate and Ethylenediaminetetraacetic acid) and 1M NH_4NO_3 (DIN 19730 2009) according to the German law (BBodSchV 1999).

The pseudo-total contents of heavy metals in aqua regia extracts were measured with an atomic absorption spectrometer (AAS) (MSeries, Thermo, at the Faculty of Agricultural and Veterinary-University of Prishtina) by the flame method. For determination of exchangeable and mobile forms of metals inductively coupled plasma optical emission spectrometry (ICP-OES; Varian 720ES) at Justus Liebig University (JLU) was used due to its higher sensitivity compared to the AAS flame methodology.

For quality assurance certified reference materials ("soil 1" and "soil 2", test 2004, 2005) supplied by the "Centre for Agricultural Technology Augustenberg" (Karlsruhe) were used for measurement of heavy metals in aqua regia extract and internal reference material (JLU) was used for plant available and mobile forms of heavy metals. Also, 10% of total samples were additionally extracted and analyzed at JLU.

2.4. Data analysis

Descriptive statistics analysis and multiple regression analysis were performed using Minitab (Statistical Software version 16).

3. RESULTS AND DISCUSSION

Table 2 shows the main descriptive statistic indexes for 21 analyzed parameters (pH_{H20}, pH_{CaCl2}, OM, Ni_{AR}, Ni_{EDTA}, Ni_{AN}, Zn_{AR}, Zn_{EDTA}, Zn_{AN}, Cu_{AR}, Cu_{EDTA}, Cu_{AN}, Cr_{AR}, Cr_{EDTA}, Cr_{AN}, Cd_{AR}, Cd_{EDTA}, Cd_{AN}, Pb_{AR}, Pb_{EDTA}, Pb_{AN}) in agricultural soils of Kosovo. Most of elements (Ni, Zn, Cu, Cr, Cd, Pb) show a wide range of concentrations, and their mean levels reach 1.5 to 2.5 times of those of their median values.

3.1. **Pseudo total contents for distinct heavy metals in agricultural soils**

3.1.1. Lead

Pb concentrations vary from 15.6 to 2206.3 mg kg^{-1}, with a mean 163.3 mg kg^{-1} and a significantly lower median (60.1 mg kg^{-1}). 5 % of analyzed samples showed a very high concentration over 1000 mg kg^{-1}, while 9 % of samples surpassed the critical limit concerning the EU standards (300 mg kg^{-1}, EC 1986).

Table 2. The main descriptive statistics of the analyzed parameters

Variable	Mean	SE Mean	StDev	Min	Q1	Median	Q3	Max
pH_{H20}	7.0674	0.0503	0.5666	5.66	6.56	7.09	7.61	8.02
pH_{CaCl2}	6.7261	0.0497	0.5596	5.42	6.25	6.87	7.2	7.78
OM(%)	6.794	0.205	2.309	2.472	5.085	6.541	8.381	15.918
$Ni_{AR\ (mg\ kg^{-1})}$	156.5	26	293	12.5	49.4	103.4	161.2	2864
$Ni_{EDTA\ (mg\ kg-1)}$	8.047	0.75	8.447	0.636	2.779	5.645	10.416	60.095
$Ni_{AN\ (mg\ kg-1)}$	0.512	0.105	1.179	0.013	0.06	0.13	0.442	9.865
$Zn_{AR\ (mg\ kg-1)}$	90	12.9	145.3	14.5	38.1	56	78.6	1284.1
$Zn_{EDTA\ (mg\ kg-1)}$	9.71	3.24	36.46	0.6	1.7	2.28	4.12	372.87
$Zn_{AN\ (mg\ kg-1)}$	0.2595	0.0522	0.5879	0.001	0.021	0.0627	0.1888	4.0397
$Cu_{AR\ (mg\ kg-1)}$	33.35	1.25	14.05	9.36	23.29	31.08	39.43	92.65
$Cu_{EDTA\ (mg\ kg-1)}$	5.806	0.326	3.671	1.511	3.568	5.133	6.73	26.61
$Cu_{AN\ (mg\ kg-1)}$	0.0449	0.0048	0.05415	<ND	0.0193	0.0346	0.0545	0.4602
$Cr_{AR\ (mg\ kg-1)}$	92.3	12.2	137.5	17.3	45.1	67.4	102.8	1444.7
$Cr_{EDTA\ (mg\ kg-1)}$	0.0799	0.0044	0.0492	0.0244	0.0467	0.0645	0.0974	0.2989
$Cr_{AN\ (mg\ kg-1)}$	0.0071	0.0003	0.0033	0.0022	0.0049	0.0067	0.0086	0.0236
$Cd_{AR\ (mg\ kg-1)}$	1.005	0.129	1.458	0.036	0.521	0.661	0.87	14.16
$Cd_{EDTA\ (mg\ kg-1)}$	0.2742	0.0762	0.8591	0.0292	0.0737	0.0999	0.1455	9.0367
$Cd_{AN\ (mg\ kg-1)}$	0.009	0.0021	0.0232	<ND	0.0009	0.0024	0.0071	0.2106
$Pb_{AR\ (mg\ kg-1)}$	163.3	30.1	338.7	15.6	43.6	60.1	92.5	2206.3
$Pb_{EDTA\ (mg\ kg-1)}$	41.2	10.5	118.4	1.8	6.8	10.1	13.9	870.3
$Pb_{AN\ (mg\ kg-1)}$	0.115	0.0228	0.2568	0.0089	0.052	0.0787	0.1058	2.8702

ND - Not detected, Mean - arithmetic mean of soil samples, SE Mean - Standard error of the mean, StDev - standard deviation, Min – minimum, Q1 – firs quartile, Median – median of soil samples, Q3 – third quartile, Max – maximum

Taking into account the permitted values in Kosovo (50 mg kg^{-1}, administrative instruction 2009), and Germany (100 mg kg^{-1}, BMU 2007, 1992; BBodSchV 1999), 67% respectively 23% of samples exceeded the permitted values (Fig. 2). Similar values on high levels of Pb in some areas of Kosovo, mainly around the contamination sources, have been reported also by other authors: For instance, Nannoni et al., (2011) determined high levels of Pb from 53.4 to 5536 mg kg^{-1}, Borgna et al. (2009) 49.9 to 37123 mg kg^{-1}, Elezi & Jusufi (1996) 235 to 7500 mg kg^{-1}. However, studies on agricultural areas situated far from contamination sources reported lower values for Pb. Thus, Maxhuni et al., (2011), report levels from 1.9 to 173.7 mg kg^{-1} of Pb in the root system zone, depending on the distance from roads.

3.1.2. Nickel

Concentrations of Ni range from 12.5 to 2864 mg kg^{-1}, with a mean of 156.5 mg kg^{-1} and a significantly lower median (103.4 mg kg^{-1}). 5 % of analyzed samples showed a very high concentration over 400 mg kg^{-1}, whereas 62 % of samples exceeded the critical limit set by the EU standards (75 mg kg^{-1}, EC 1986). Regarding the limit of permitted values in Kosovo and Germany (50 mg kg^{-1}, administrative instruction 2009; BMU 2007, 1992; BBodSchV 1999), 74 % of samples exceeded that limit (Fig. 2). Similar values for high levels of Ni in some areas in Kosovo, mainly around the contamination sources, have also been reported by Borgna et al., (2009), who determined levels of Ni from 12.3 to 2842 mg kg^{-1}.

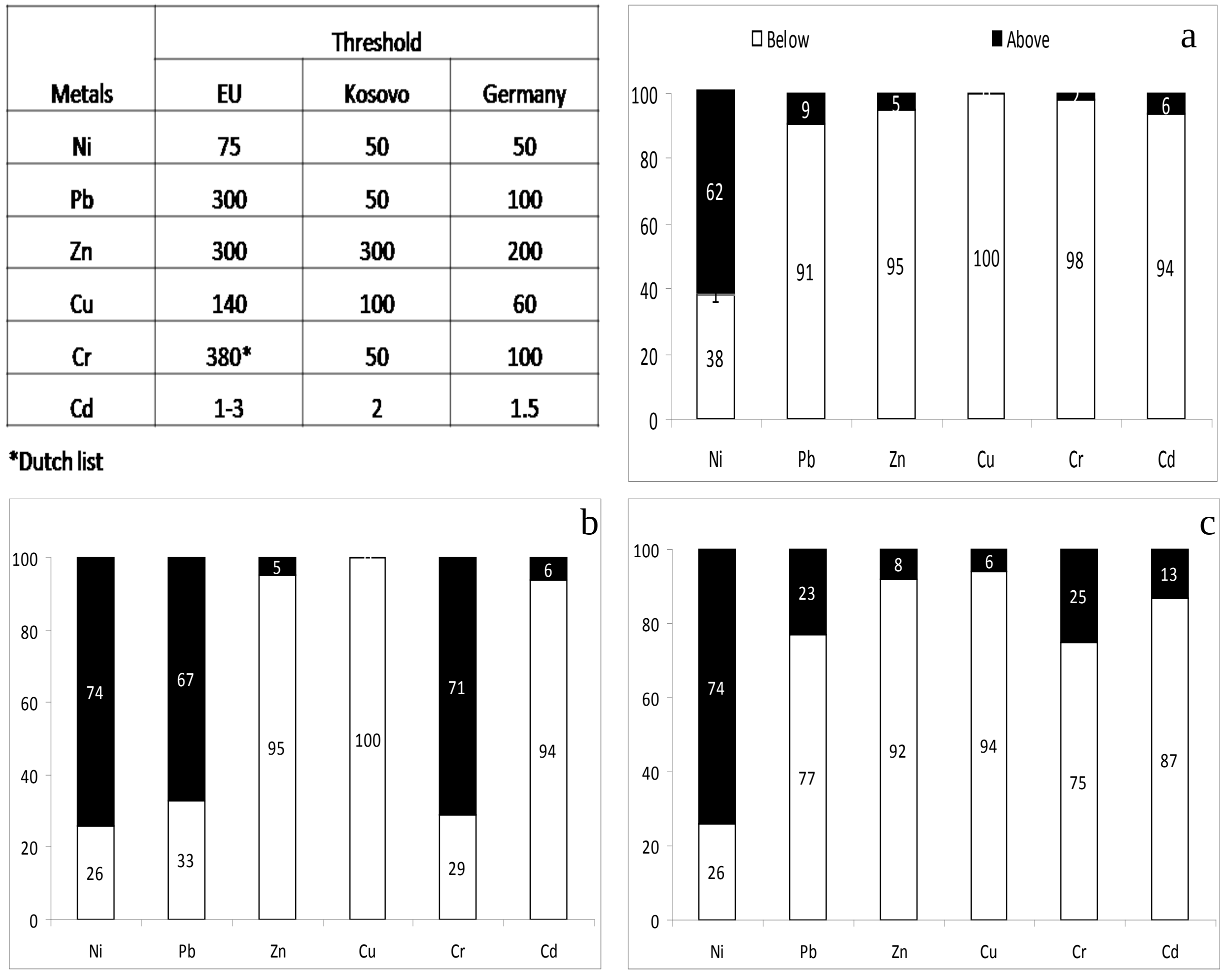
3.1.3. Zinc

The content of Zn varies from 14.5 to 1284.1 mg kg^{-1}, with a mean of 90.0 mg kg^{-1} and a significantly lower median (56.0 mg kg^{-1}) (Table 2). Only 5 % of samples exceeded the critical limit as to EU standards and that of Kosovo (300 mg kg^{-1}, EC 1986; administrative instruction 2009). Compared to the limit values in Germany (200 mg kg^{-1}, BMU 2007, 1992; BBodSchV 1999), 8 % of samples exceeded it (Fig. 2). Similar values of high levels of Zn in some areas in Kosovo, mainly around the contamination sources, have also been reported by Borgna et al., (2009) who determined levels of Zn from 31.7 to 17239 mg kg^{-1}. Similarly, Elezi & Jusufi (1996) reported values from 150 to 7000mg kg^{-1}.

3.1.4. Cadmium

The content of Cd also showed high variations from 0.036 to 14.16 mg kg^{-1}, with a mean of 1.005 mg kg^{-1} and median of 0.661 mg kg^{-1} (Table 2). Only 6 % of samples exceeded the critical limit as to EU standards and Kosovo's standards (3 mg kg^{-1}, EC, 1986, 2 mg kg^{-1} administrative instruction, 2009). Regarding the legislation for soils in Germany (BMU 2007, 1992; BBodSchV 1999), 13 % of samples exceeded the limit of 1.5 mg kg^{-1} (Fig. 2).

Similar values on high levels of Cd in some areas in Kosovo, mainly around the contamination resources, have been reported by other authors as well.



Metals	Threshold EU	Threshold Kosovo	Threshold Germany
Ni	75	50	50
Pb	300	50	100
Zn	300	300	200
Cu	140	100	60
Cr	380*	50	100
Cd	1-3	2	1.5

*Dutch list

Figure 2. Percentage of the total amount of heavy metals (mg kg^{-1}), which are under or above the acceptable levels, according to different countries, a) European Union, b) Kosovo, c) Germany.

Nannoni et al., (2011) report the high level of Cd from 0.36 to 11.8 mg kg^{-1} and Borgna et al., (2009) from 0.37 to 69.7 mg kg^{-1}.

3.1.5. Copper

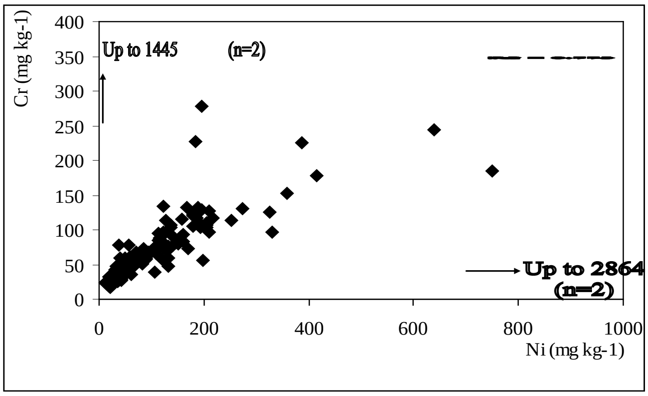
Concentration of Cu revealed variations from 9.36 to 92.65 mg kg^{-1}, with a mean of 33.35 mg kg^{-1} and a median of 31.08 mg kg^{-1} (Table 2). All analyzed samples have been below the critical limit regarding the EU standards and that of Kosovo (140 $mgkg^{-1}$, EC 1986; 100 $mgkg^{-1}$, administrative instruction 2009). Regarding permitted values in Germany (BMU 2007, 1992; BBodSchV 1999), 6 % of samples were above the limit of 60 mg kg^{-1} (Fig. 2). Other authors also reported similar values of Cu levels concerning some areas in Kosovo. Nannoni et al., (2011) measured levels of Cu from 17.8 to 134 mg kg^{-1} and Borgna et al., (2009) from 2 to 563.4mg kg^{-1}.

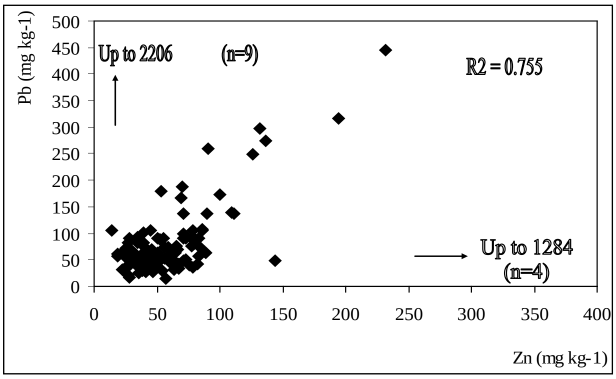
3.1.6. Chromium

In the analyzed samples, the content of Cr showed high variations from 17.3 to 1444.7 mg kg^{-1}, with a mean of 92.3 mg kg^{-1} and median 67.4 mg kg^{-1} (Table 2). Only 2 % of samples exceeded the critical limit regarding the Dutch list (380 mg kg^{-1}, 1996). Concerning the permitted values in Kosovo (50mg kg^{-1}, administrative instruction 2009), and Germany (100 mg kg^{-1}, BMU 2007, 1992; BBodSchV 1999), 71% respectively 25% of samples were above limit (Fig. 2). Similar values of high levels of Cr in some areas in Kosovo, mainly around the contamination sources, have also been reported by other authors. Borgna et al., (2009) determined high level of Cr from 24.9 to 5497 mg kg^{-1}.Correlation of pseudo-total concentration among Ni and Cr (R^2=0.773) and Zn and Pb (R^2=0.7554), are given in figure 3. This type of correlation has not been noticed among other metals.

3.2. EDTA extractable (potential plant available) heavy metals in soil

Many authors consider EDTA a suitable extractant to assess the potential plant availability of most heavy metals for plant uptake (Norvell 1984; Kociałkowski et al., 1999; Kabala & Singh 2001, Damian et al., 2008).





n= number of samples above the values

Figure 3. Correlation between heavy metals

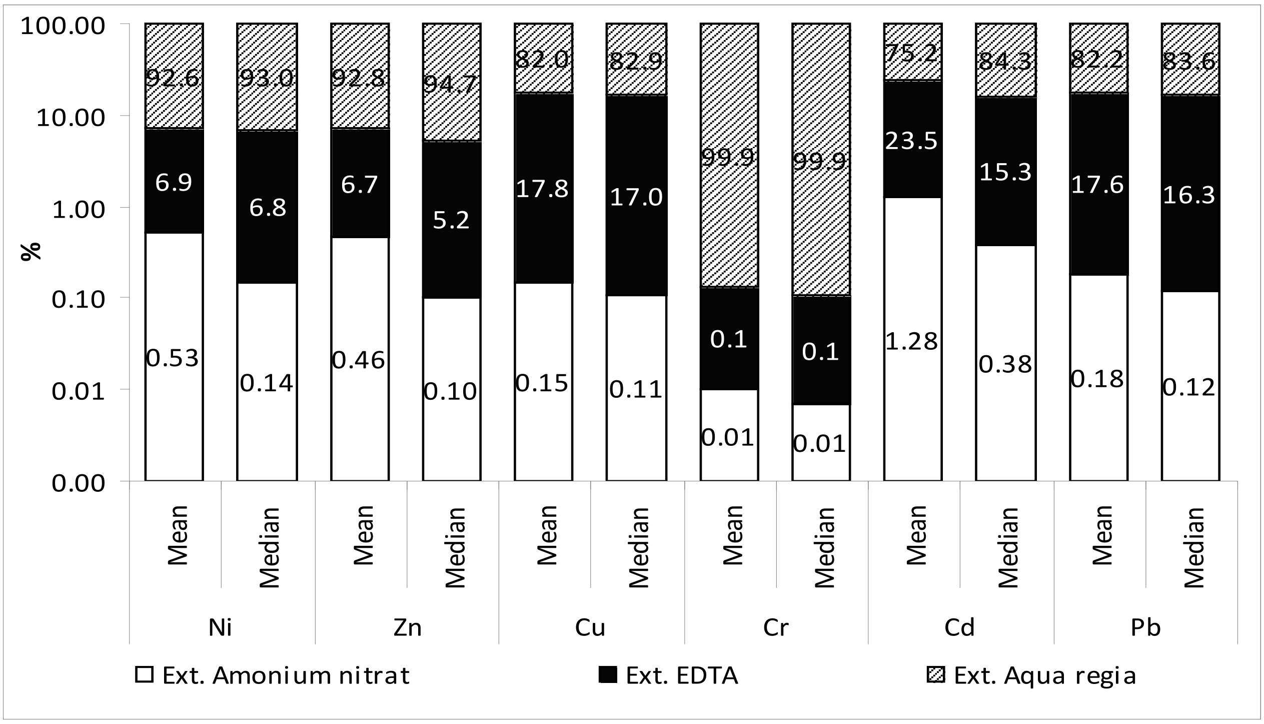


Figure 4. The distribution of Ni, Zn, Cu, Cr, Cd and Pb in the differently extracted fractions.

Table 3.The relationship between EDTA- extractable heavy metals and other properties

Regression equation								R^2
Ni_{EDTA} =	18.7	+	0.0227 Ni_{AR}	+	0.255 OM	-	2.26 pH_{H20}	0.616***
(T)	2.96**		13.5***		1.03		-2.27	
Zn_{EDTA} =	23	+	0.238Zn_{AR}	-	1.27 OM	-	3.07 pH_{H20}	0.882***
(T)	1.53		30.31***		-2.16		-1.55	
Cu_{EDTA} =	5.86	+	0.156Cu_{AR}	+	0.143 OM	-	0.881 pH_{H20}	0.352***
(T)	1.64		7.28***		0.99		-1. 53	
Cr_{EDTA} =	0.12	+	0.000216 Cr_{AR}	-	0.00124 OM	-	0.00731 pH_{H20}	0.348***
(T)	2.51		8.04***		-0.66		-0.97	
Cd_{EDTA}=	0.14	+	0.242 Cd_{AR}	-	0.0019 OM	+	0.004 pH_{H20}	0.169***
(T)	-0.01		4.98***		-0.05		0.03	
Pb_{EDTA} =	8.2	+	0.331Pb_{AR}	-	1.36 OM	-	1.66 pH_{H20}	0.889***
(T)	0.17		31.24***		-0.74		-0.22	

EDTA (metals are extracted with EDTA), AR (metals are extracted with Aqua Regia), T- Student's t-test

*, ** and *** indicate significant at 5, 1 and 0.1% confidence level, respectively.

The potential plant availability of heavy metals in soil was assessed using a "potential bioavailability factor (PBF)" calculated on the basis of the following equation:

$$PBF = \frac{M_{(EDTA)}}{M_{(AR)}} \text{x} 100 \quad (1)$$

Where $M_{(AR)}$ is the pseudo total metals concentration in soil and $M_{(EDTA)}$ is the EDTA extractable of metals in soil. On the basis of the PBF, Cu was extracted by EDTA in highest amount, from 5.72 to 57.92 %, with a mean of 17.84 % and median of 16.99 % (Fig. 4.). The lowest extraction efficiency was encountered for Cr, from 0.02 to 0.63%, mean of 0.12 % and median of 0.098 %. Other metals show the following mean values:

Pb 17.63, Cd 23.48, Ni 6.88, Zn 6.71 %. The median values are: Pb 16.27, Cd 15.3, Ni 6.84 and Zn 5.16% (Fig. 4). Extractability by EDTA follows this order: Cu ≈ Pb ≈ Cd >> Ni ≈ Zn >> Cr. Similar results have been reported by other authors (Ashraf et al., 2012; Abdu et al., 2012; Nanoni et al., 2011; Takac, et al., 2009; Mitsios 2005; Abollino et al., 2002). The influence of total content on the EDTA extracted amount of heavy metals is given in table 3. The content of organic matter and pH showed no significance for all metals.

3.3. Ammonium nitrate extractable (mobile) heavy metals in soil

The mobile fraction of heavy metals in soil was, analogous to PBF, assessed using a "mobile factor (MF)" calculated on the basis of the following equation:

$$MF = \frac{M_{(AN)}}{M_{(AR)}} \text{x} 100 \quad (2)$$

Where $M_{(AR)}$ is the pseudo-total metals concentration in soil and $M_{(AN)}$ is the ammonium nitrate extractable fraction of metals in soil. On the basis of MF, Cd was extractable in high percentages, up to 24.48%, with a mean of 1.28 % and a median of 0.376% (Fig. 4). A lower percentage was encountered for Cr, from 0 to 0.02%, with a mean of 0.01 % and a median of 0.007%. The other metals showed the following mean values: Ni 0.53, Pb 0.18, Cu 0.15 and Zn 0.46%. Median values are: Ni 0.144, Pb 0.122, Cu 0.11 and Zn 0.103 % (Fig. 4). Thus, the range concerning the extractability of the different metals by NH_4NO_3 resulted as follows: Cd >>Ni>Pb>Cu>Zn>>Cr.

According to BBodSchV (1999) (0.1 mg kg^{-1}), 29 % of all investigated samples exceeded the limit values for Pb, 6 % for Ni (1.5 mg kg^{-1}), 3% for Zn (2 mg kg^{-1}), 1.5 % for Cd (0.1 mg kg^{-1}) and 0.8% for Cu (1 mg kg^{-1}). Similar results have also been reported by other authors (Pueyo et al.; 2004; Mellum et al., 1998). For the amount of heavy metals extracted with NH_4NO_3, the soil pH and the content of heavy metals extracted with EDTA (Table 4) played an essential role. Total metal content showed positive regression only for Ni at a confidence level of 0.1%.

Similar results were shown by Mellum et al., (1998), who did not find significance between the samples extracted with aqua regia and those extracted with DTPA. A positive regression with extracted metals by EDTA was determined for Ni, Zn and Cd (0.1 % significance level), while there was no significance for Cr, Cu and Pb. The impact of pH on NH_4NO_3 extractable amounts was highly significant for Ni, Zn, Cd and Pb (0.1 % significance level), whereas there was no significance for Cu and Cr.

Table 4. The relationship between NH_4NO_3- extractable heavy metals and other properties

Regression equation										R^2
Ni_{AN} =	4.27	+	0.00179 Ni_{AR}	+	0.0524 Ni_{EDTA}		0.0223 OM	-	0.609 pH_{H20}	0.622***
(T)	4.69***		4.89***		4.18***		-0.64		-4.31***	
Zn_{AN} =	2.87	+	0.000767Zn_{AR}	+	0.00855 Zn_{EDTA}	-	0.0078 OM	-	0.383 pH_{H20}	0.633***
(T)	6.60***		1.17		3.32***		-0.46		-5.58***	
Cu_{AN} =	0.0028	-	0.000354 Cu_{AR}	+	0.0018 Cu_{EDTA}	+	0.00361 OM	+	0.0027 pH_{H20}	0.037
(T)	0.04		-0.77		1.1		1.39		0.26	
Cr_{AN} =	0.0112	-	0.000004 Cr_{AR}	+	0.0159 Cr_{EDTA}	+	0.000016 OM	-	0.000737 pH_{H20}	0.061
(T)	2.88*		-1.46		2.21		0.11		-1.22	
Cd_{AN} =	0.0856	-	0.000749 Cd_{AR}	+	0.0235 Cd_{EDTA}	-	0.00024 OM	-	0.0114 pH_{H20}	0.801***
(T)	6.48***		-1.06		19.64***		-0.49		-5.77***	
Pb_{AN} =	1.22	-	0.000092Pb_{AR}	+	0.000313 Pb_{EDTA}	+	0.0119 OM	-	0.168 pH_{H20}	0.109**
(T)	4.17***		-0.47		0.56		1.04		-3.62***	

AN (metals are extracted with NH4NO3), AR (metals are extracted with Aqua Regia), EDTA (metals are extracted with EDTA), T- Student's t-test, *,** and *** indicate significant at 5, 1 and 0,1% confidence level, respectively.

4. CONCLUSIONS

In most of the soils under investigation total content of heavy metals in agricultural soils of Kosovo are within the permitted values given by the EU. Nevertheless 62% of all soil samples exceeded the limit value of total concentration of Ni. The potential bioavailable and mobile fractions of this element was determined at 6.84 and 0.144% respectively.

High concentrations of heavy metals have been noticed near contamination sources (mainly near metals' industries), which, in some cases, have exceeded many times the allowed limits. Moreover, the potential bioavailable form of metals around these sources has shown very high values, presenting a serious hazard for human health, since these soils are being cultivated and their products being consumed.

Cu has been the only metal which did not exceed the limit of permitted level for total concentration regarding EU standards.

The regression analysis has shown that the pseudo-total metal content significantly influenced ($p<0.001$) the amount of metals extracted with EDTA. The content of organic matter and the value of pH did not show any significance in the amount of extracted metals with EDTA.

Strong correlation ($p<0.001$) between soil pH value and mobile Ni, Zn, Cd and Pb has been shown. Correlation of potential bioavailable metal contents with mobile fractions did show significance ($p<0.001$) for Ni, Zn and Cd, as well as for Cr on a significance level of $p<0.05$. The pseudo-total metal content was significant ($p<0.001$) only for mobile Ni.

Based on the results of investigated soil samples and on the necessity for human health protection, the investigation on heavy metals concentrations in agricultural products of the Kosovo is an urgent and indispensable task and would fill a gap not met in the literature so far.

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