Concentration of Selenium and Other Minerals and Their Relationship in Soils and Fodder Plants in Kosovo

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***Abstract*—Minerals play many important functions in plant and animal metabolism. Therefore, we investigated the concentration of Se and other minerals and their relationships in soils and fodder plants in Kosovo. Seventy-three samples of each soil and fodder plants (grass, maize, and wheat) from 30 farms were collected. After processing and digestion, soil and plant samples were analyzed for mineral concentration by ICP-MS. Mineral concentrations in soil and fodder crops, and the best predicting/explanatory models for micro minerals concentration, achieved by stepwise linear regression, are presented. Results showed very low concentration of Se in most of the soil and all fodder samples. In addition, the concentration of Co, Zn and Fe was not sufficient to satisfy requirements for all categories of farm animals. Plant Se concentration showed a positive relationship with Se concentration in soils. Plant Zn, Mo, Mn, Fe and Pb, in general, showed no significant relationship with their concentration in soil, while plant Co and Cd showed positive relationship only in maize, and Cu in wheat grain. Among the soil properties, pH had the highest effect on the concentrations of Co, Mo, Mn, Cd and Pb in fodder crops.**

***Keywords*—micro minerals, selenium, deficiency, soil-plant relationship, Kosovo**

I. INTRODUCTION

Micro minerals, known also as trace elements, although found in small concentrations, play very important functions in plant and animal metabolism. Most of them are essential nutrients for plants or animals. However, in excessive amounts, they may become toxic. Most of the micro minerals considered essential for plants are also essential for animals and humans, with minor exceptions. For example, selenium (Se) and cobalt (Co) are essential micro elements for animals and humans, but they are considered only beneficiary elements for plants, especially for Se hyperaccumulators (Se) and for leguminous plants (Co) [1, 2]. Total concentrations of micro minerals in soils worldwide vary greatly because soil minerals are derived from parent material of different geological origins. However, plant availability of micro minerals does not depend on the total concentration in soils only. Various soil factors, such as pH, redox potential, aeration, temperature, Soil Organic Matter (SOM), concentrations of the other minerals and their chemical compounds can affect mineral concentration in the soil solution and plant availability [3]. Therefore, the knowledge about the total micro mineral concentrations in soil in relation to other soil properties is essential to predict status of micro minerals in plants and to avoid mineral deficiency and toxicity in plants and animals.

Micro mineral concentrations in soil and plants and their relations with animal health are described widely in the literature worldwide. Selenium in soil is at low concentration in major areas in Europe (2). An overview on micro mineral concentrations reported by Manojlovic and Singh [4] revealed low concentration of Se in soils and plants in most of the Balkan regions, and furthermore, low concentration of copper (Cu) and zinc (Zn) in some areas. There is very scarce knowledge on micro mineral concentration in soils and plants of Kosovo. In two previous studies [5, 6], the concentrations of Se and other major and micro minerals in the feed supplied to sheep and cows and in the blood of these animals were found to be inadequate in the greater proportion of samples analyzed.

Macro minerals concentrations in soil and fodder plants are important for both plant and animal nutrition and growth. Concentrations of macro minerals in soil are reported to affect the uptake of other micro and macro minerals in plants [3]. A soil pH between 5.5 and 7.5 is required for maximum yield in most of agricultural crops and for maximal nutrient availability [7–9].

The present study investigated the concentrations of Se and other micro and macro minerals in soils and in selected fodder plants in Kosovo in relation to animal requirements. The second objective was to investigate the relationship of micro mineral concentrations in soils and fodder plants.

II. MATERIAL AND METHODS

A. Study Area

The experimental study consisted of 30 farms in different districts of Kosovo. Kosovo is situated in the Western Balkans with a geographical area 10 908 km^2. It is divided into two main agricultural regions, Dukagjini Plain and Kosovo Plain, surrounded by hilly and mountainous areas. The average altitude in Kosovo is 810 m above sea level, ranging from 270 to 2656 m above sea level. Kosovo has a mid-continental climate, with an average annual rainfall of 596 mm and average annual temperature 10°C [10, 11]. Geological base in Kosovo is rather complex and it results with diverse soil types even in such small area. Fluvisols are the main soil types in plains, while in hilly areas around the plains Vertisols, Cambisols and Regosols are widespread. According to an agricultural holdings survey provided by Kosovo Agency of Statistics (KAS), total utilized area of agricultural land in 2017 was 416 072 ha with 53% meadows and pastures, and 45%) arable land [12]. Grain cereals accounted for 120 746 ha (65%) of the arable land, followed by forage crops with 35.999 ha (19%).

B. Sample Collection

A total of 73 plant samples were collected, of which: 27 grass, 24 maize and 22 wheat samples. In addition, an equal number of soil samples was collected from the same site as the plant sample. Three replicates for each soil and plant sample were collected at different sites of each field, to avoid spatial and other differences, and each replicate was collected within a square meter area. To avoid differences in age variability and chemical composition, only young grass samples were collected. Whole plant maize samples were collected at the vegetative growth stage (between V8 and V12) and cut in small pieces for better drying for further processing. Wheat samples were collected at harvesting time and grains were separated from straw. Both grain and straw were analyzed for minerals. Soil samples were collected by soil auger from 0 to 30 cm depth, while plant samples were cut with hand clippers. Soil and plant samples were placed in paper bags and air dried at 40°C for three days. Plant samples were further dried at 105°C for dry matter determination. Both soil and plants samples were ground finely before analysis.

C. Sample Digestion and Chemical Analysis

Dried plant and soil samples (250 mg each) were used for analysis. Plant samples were digested using 2 ml of ultrapure water and 5 ml of concentrated nitric acid in Ultra Clave (Milestone Inc.). Soil samples were digested the same way as plants, but 1 ml of hydrofluoric acid was also used in addition to nitric acid. An internal standard containing 4 mg/L indium, thallium, tellurium, and rhodium was added to each sample prior to digestion. After digestion, the plant samples were diluted up to 50 ml with ultrapure water, while the soil samples were diluted up to 500 ml (tenfold higher dilution for soil samples was done because concentrated hydrofluoric acid can damage the columns of the instrument). All samples were left for stabilization at least overnight before their analysis. Total mineral concentration in all digested samples of plant and soil was determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent Technologies 8800 series), and oxygen was used as a reaction gas in the collision cell.

Different soil and plant Certified Reference Materials (CRMs), such as Soil DC73324, Wheat Flour 1567a, and Apple Leaves 1515; prepared the same way as other samples, were analyzed and used for the quality control of the analytical method, and their concentrations were within the certified ranges. Blank samples were prepared in each set of samples, and the Limit of Detection (LOD) was calculated as 3 × Standard Deviation (SD) of the blanks and Limit of Quantification (LOQ) as 10 × SD of the blanks. No mineral concentrations were below LOQ in any sample.

D. Analysis of soil pH, Total Carbon (C) and Total Nitrogen (N)

Soil pH was determined electrometrically in soil-to-water ratio of 1:2.5 suspension. Ten grams of air-dry soil was mixed with 25 ml of distillated H_2O and after 30 min pH was measured with pH meter (pHM240 pH/ion meter-Radiometer).

Determination of total C was performed following the “dry combustion” method proposed by Allison, which is described by Nelson and Sommers [13]. About 200 mg of finely ground soil samples were weighed in tin foil and samples were analyzed on the Leco CHN 1000 analyzer. During the analysis at 1050°C the samples became completely combusted and all carbon oxidized to CO_2. The concentration of CO_2 gas was measured vs. infrared light (IR cell).

Determination of total N was performed according to the Dumas method, as it was described by Bremner and Mulvaney [14]. The principle is the same as for total C, but here the Nitrogen Oxide compounds (NOx) were reduced by the use of copper to N_2. The concentration of nitrogen gas is then measured by thermal conductivity (TC cell) on the same analytical instrument, Leco CHN 1000.

E. Data Processing and Statistical Analysis

For descriptive statistics and other data processing, R statistical program, version 3.0.1, R Commander version 2.0-4 were used. Tukey’s HSD at level of significance 0.05 was used to test the difference in means among plant types. Stepwise linear regression was employed to test the effect of soil properties on mineral concentration in plants. Regression analyses were done in the way that initially all soil factors were included in the model, and later by using stepwise model selection, non-significant factors were removed and only those significant left in the model. Therefore, the regression models in Table 4, present the best predictors for the mineral concentration in plants. The R^2 values (%) in Table 4 stand for the model and not for a particular relationship.

III. Results and Discussion

A. Concentration of Micro Minerals in Soil and Plants

Soil Se at different locations in Kosovo ranged from 110 to 500 µg kg^{-1}, with a mean concentration 270 µg kg^{-1} (Table 1). While Se concentration in plants derived from the respective soils ranged between 5 and 97 µg Se kg^{-1} (Table 2). Our results are similar to those reported from other researchers on soil Se in the Balkans region [4, 15]. In addition, the mean concentration of Se was significantly higher in grass compared with maize, wheat grain, and straw (Table 3). Selenium is not essential for normal plant growth; although it is considered that it might be essential or beneficial for algae and Se-accumulator plants [3, 16]. However, Se is essential for animals and humans [2, 17]. Adequate Se concentration in soil is important to ensure adequate concentration in plants. It is suggested that soils containing less than 500 µg Se kg^{-1} produce plants with insufficient level of Se for human and animal nutrition, while soil Se below 100 µg Se kg^{-1} is related with endemic diseases such as Keshan Disease (a congestive cardiomyopathy) and Kashin-Back Disease (an osteochondropathy) [18]. Requirements for Se in animal’s range between 100 and 300 µg Se kg^{-1} diet, and Se concentration lower than 50 µg kg^{-1} diet is considered deficient [19, 20]. Therefore, considering Se concentration in fodder plants from Kosovo, most of the samples were found to be deficient in Se. Only four out of 73 samples were at marginal level, and none of the plant samples was sufficient to meet the animal requirements.

Zinc concentration in soil ranged between 30 and 140 mg kg^{-1} with a mean of 78 mg kg^{-1}, except for a single sample with very high concentration (1400 mg kg^{-1}) close to a magnesite mining area in Strezovce (Table 1). Zinc concentration in the selected fodder plants ranged between 2.3 and 116 mg kg^{-1} with a mean of 31 mg/kg (Table 2). Zinc mean concentration was significantly higher in maize (46 mg kg^{-1}), than in grass (32 mg kg^{-1}) and wheat grain (34 mg kg^{-1}), and significantly lower in straw (11 mg kg^{-1}) (Table 3). Zinc is essential for both plants and animals/humans, and studies indicate that nearly half of the world population suffers from Zn deficiency [21]. Its deficiency in animals occurs most often in regions with Zn deficient soil. However, also other factors than soil Zn concentrations affect its concentration in plants and its bioavailability in animals. For instance, phytic acid inhibits Zn uptake in monogastric animals [22–24]. Considering that the requirements for ruminants range between 20 and 73 mg kg^{-1} [19], it is obvious that all straw samples were deficient or inadequate in Zn. The knowledge of Zn concentration in straw is important because many beef cattle farmers use straw as substitute for grass, while using high amounts of cereal grains.

Although wheat grain, grass, and maize contained adequate concentration of Zn for different categories of ruminants, Zn concentration may not be sufficient for early-lactating dairy cows, swine and chicken [19].

Copper in soil ranged between 14 and 78 mg kg^{-1}, with a mean concentration of 28 mg kg^{-1} (Table 1). Plant Cu ranged between 1.4 and 12.3 mg kg^{-1}, with mean concentration 6.2 mg kg^{-1} (Table 2). Both soil and plant concentrations are quite similar with those reported by Manojlovic and Singh [4] and Vejnovic *et al.* [15] for Balkan region and those reported worldwide [3]. Copper mean concentration was significantly higher in maize and grass (8.7 and 8.3 mg kg^{-1}), than in wheat grain (4.2 mg kg^{-1}) and the lowest concentration was in wheat straw (2.2 mg kg^{-1}) (Table 3). The concentrations reported here are below the mineral requirements for ruminants [19], which ranged from 7–11 for sheep and 9–18 for different categories of cattle. Furthermore, none of the wheat grain or straw samples reached the concentration required for animals. Although grass and maize were within the requirement limits for sheep, only a few samples met the requirements for mid-lactating cows (12–18 mg kg ^{1}).

Soil Co ranged between 8 and 64 mg/kg with a mean concentration of 23 mg/kg (Table 1). This is higher than the world average concentration of 10 mg kg^{-1} reported in the literature [3]. Plant Co ranged between 0.01 and 1.07 mg/kg with an average concentration of 0.09 mg/kg (Table 2). There was no significant difference in plant Co among different plant species (Table 3). Considering that animal requirements for Co are between 0.1 and 0.2 mg kg^{-1} of feed, only about 29% of plant samples were sufficient in Co. Therefore, Co supplementation seems to be necessary for ruminants on majority of the farms, as ruminants need Co for synthesis of cobalamine (vitamine B_{12}) from ruminal bacteria, in contrast with non-ruminants which only can utilize synthesized cobalamin [19, 20, 25].

Soil Mo was found to range between 0.4 and 3.2 mg kg^{-1}, with a mean concentration of 1.3 mg kg^{-1} (Table 1). This mean value is close to the estimated world average of Mo of 1.1 mg kg^{-1} [3]. Molybdenum concentration in plants ranged between 0.02 and 2.60 mg/kg, with a mean concentration 0.56 mg kg^{-1} (Table 2). Grass was significantly higher in Mo than maize, wheat grain, and straw (Table 3). Molybdenum concentration in feed above 0.5 mg kg^{-1} is recommended for animals [19, 25]. In addition, Mo is also important for plants, and adequate concentration in most of plants ranges between 0.2 and 5 mg kg^{-1}, except for some leguminous plants which require more Mo [3]. Therefore, results about Mo concentration in plants, indicate possible Mo deficiency in Kosovo for both plant and animal health.

Manganese in soil ranged from 240 to 3100 mg kg^{-1}, with a mean concentration of 1000 mg kg^{-1} (Table 1). The mean concentration of soil Mn is higher than the worldwide average concentration of 488 mg Mn kg^{-1} [3]. Manganese in plants ranged from 10 to 460 mg kg^{-1}, with a mean concentration of 67 mg kg^{-1} (Table 2). Kabata-Pendias [3] suggested that critical deficiency levels for most plants range between 15 and 25 mg kg^{-1} and that plants may be negatively affected at concentration above 400 mg kg^{-1}. Based on these suggestions, only few straw samples were at critical deficiency levels for plants, but two grass samples were found to exceed the optimal Mn level for plant health. However, it is reported previously that Fe and Mn are interrelated in their metabolic functions, and an appropriate ratio in plants is necessary for healthy plants [3]. The Fe:Mn ratio in plants should range from 1.5 to 2.5, and at lower ratio, symptoms of Mn toxicity and Fe deficiency may occur in plants, while the opposite is true for the higher ratio [3]. In the present study, 57% of plant samples had Fe:Mn ratio below 1.5 and about 23% of them had the Fe:Mn ratio above 2.5. Ruminant requirement for Mn range between 12 and 40 mg kg^{-1}, and the maximum tolerable level is at 2000 mg kg^{-1} [19, 25]. Manganese in grass was significantly higher than in wheat grain and straw, but not significantly higher than in maize (Table 3).

Iron concentration in **s**oil ranged between 12 to 53 g kg^{-1}, with a mean concentration of 30 g kg^{-1} (Table 1). The mean is slightly lower than world average concentration for Fe (35 mg kg ^{1}), and it is within the common worldwide range [3]. Iron concentration in plants varied widely between 14 and 560 mg kg^{-1} (Table 2), being significantly higher in grass and maize than in wheat grain and straw (Table 3). Animal requirements for Fe in different categories of ruminants were reported to range from 30 to 50 mg kg^{-1} [19], being higher for poultry (up to 80 mg kg^{-1}) and swine (up to 100 mg kg^{-1}). Based on the requirement presented above, wheat grain can be considered adequate in Fe for ruminants, but deficient for poultry and swine, as the Fe concentration in wheat grain ranged between 31 and 54 mg kg ^{1}. In addition, phytate (phytic acid), primarily present in cereal grains, is a considerable inhibitory factor for Fe absorption. This is a problem for monogastric animals such as poultry and swine which do not produce phytase, in contrast to what happens in ruminants where phytase is produced by ruminal microflora [19, 20]. Therefore, Fe supplementation for poultry and swine may be required.

Cadmium concentration in soils and plants ranged from 0.07 to 5.6 mg kg^{-1}, and 0.01 to 1.1 mg kg^{-1}, respectively (Tables 1 and 2). In general, these results are within the common ranges in soils [3]. Although there was variation of Cd concentration among and within different plants, there were no significant differences among plant species. In addition, no toxic concentration in any of the plant samples analyzed was observed, based on the maximum tolerable level for Cd (10 mg kg ^{1}) for animal feed [25].

Lead concentration in soil ranged between 16 and 2200 mg kg^{-1} with a mean concentration 78 mg kg^{-}1. The toxic level for soil Pb is reported to be above 125 mg kg^{-1} [3]. Plant Pb ranged from 0.03 to 0.83 mg/kg, with a mean concentration 0.14 mg kg^{-}1, and it was much below the maximum tolerable level for animals (100 mg kg^{-1}) suggested by NRC (2005) [25].

B. Concentration of Selected Macro Elements in Soil and Plants

Magnesium (Mg) in soil ranged from 0.6 to 21 g kg^{-1}, with a mean value of 4.4 g kg^{-1}. In plants, Mg ranged between 0.5 and 6.8 g kg^{-1} DM, with mean concentration 2.0 g kg^{-1} (Tables 1 and 2). Magnesium was significantly highest in maize, followed by grass, and the lowest concentration was found in wheat grain and straw (Table 3). Requirements for Mg in different categories of ruminants range from 0.8 to 2.9 g kg^{-1}, being the highest for early-lactating dairy caw [19]. In general, maize and grass were sufficient or higher than requirements in Mg for all categories of domestic animals, but wheat grain and straw seem to be insufficient for ruminants, particularly for lactating cows.

Soil phosphorus (P) ranged between 0.17 and 0.91 g kg^{-1}, with a mean concentration 0.50 g kg^{-1} (Table 1). Phosphorus in plants ranged from 0.2 and 6.4 g kg^{-1} (Table 2), and there was no significant difference between grass, maize, and wheat grain, except for wheat straw which was significantly lower in P (Table 3). Requirements for P in ruminants diet range between 0.5 and 4.5 g kg^{-1} [19], and it seems that most of the grass, maize, and wheat grain samples were adequate in P. A lower concentration of P in hay and maize silage in Kosovo was reported in a previous study [6].

Sulfur in soil ranged between 0.12 and 0.83 g kg^{-1} (Table 1), and its concentration in plants was from 0.5 to 5.4 g kg^{-1} (Table 2). Grass was significantly higher in S, than maize, wheat grain, and wheat straw (Table 3). Considering that the requirements for S in different categories of ruminants range between 1.4 and 2.6 g kg^{-1} [19], it seems that the most analyzed samples were adequate in S.

C. Soil pH, Total Carbon (C) and Total Nitrogen (N)

Soil pH in all our samples ranged from 4.6 to 7.9 (Table 1). Soils with pH 5.5–6.5 are classified as slightly acidic, those with pH 4.5–5.5 as moderately acidic, and those with pH < 4.5 as strongly acidic. Similarly, soil pH 7.5–8.5 is considered slightly alkaline, pH 8.5–9.5 moderately alkaline and pH 9.5 and above strongly alkaline [7, 26]. Therefore, based on the above classification, they varied from moderately acidic to slightly alkaline. In addition, it is suggested that most of agricultural crops have maximum yield in soils with pH from 5.5 to 7.5, although some crops can be grown well in higher and lower soil pH [7–9]. In the present study, 80% of the sampled soils showed soil pH between 5.5 and 7.5, while 10% was higher than 7.5, and 10% was lower than 5.5. Soil pH is important for plant yield and affects the mineral concentrations of plants. It is known that soil mobility and plant availability of most essential minerals is strongly related with soil pH [3, 7–9].

Total C in soil ranged from 0.7 to 5.0% with a mean concentration 2.2%, while total N ranged between 0.04 and 0.48% with a mean concentration 0.19%. Furthermore C: N ratio ranged between 8.5 and 19.1, with a mean ratio 11.3. Total C consists of organic C and inorganic C. Organic C or Soil Organic Matter (SOM) is frequently taken as an indicator of soil fertility. Inorganic C is generally found in highly alkaline calcareous soils. Considering that soil pH in the majority of analyzed samples was acidic or neutral (Table 1), we can assume that inorganic C was in negligible amounts and most of the soil carbon was organic C.

D. Relationship between Microelements in Plants and Soil Factors (Soil Micro and Macro Element Concentrations and pH)

To explain or predict micro mineral concentrations in plants based on soil factors a stepwise linear regression analysis was used. Table 4 presents the best prediction models obtained through stepwise regression which explain the effect of soil factors on mineral concentration in different plants.

It is reported earlier that Se uptake and its concentration in plants is dependent on a number of soil factors such as soil pH, aeration, organic matter, chemical forms of Se present in soil, and interaction with other minerals in soil [3]. In the present study, we analyzed the effect of soil pH, total C, total N, Se, and other minerals in soils on Se concentration in plants. The plant Se concentrations were mainly explained by soil Se, Mg, and S. Soil Se and Mg showed significant positive relationship with plant Se concentration, while soil S showed negative relationship (Table 4). Antagonism between S and Se is reported to be caused by the similarity in transport mechanism between sulfate and selenate ions from root to shoot [16, 27, 28]. However, the results were not the same for all plant species. For instance, soil S and Mg had no effect on Se concentration in grass, but soil Se showed positive and soil Cd negative relationship with Se concentration in grass. In addition, negative relationship between soil Fe and Mn with Se in wheat grain and wheat straw was observed, respectively. A negative correlation between soil Fe and cereal grain Se was previously reported by Johnson *et al.* [29], and they suggested possible Se immobilization by Fe minerals as reason for this relationship. In the present study, no significant effect of soil pH, total C, or total N on plant Se concentration was observed, although such effects were reported earlier in the literature [3, 28].

Plant Zn in this study was not affected by its concentration in soil. Soil Cu, Mo, S, and N positively affected Zn concentration in plants, while negative effect of soil Cd, Mn, P, and soil pH was also observed in the present study. However, these relationships were not consistent for all plant types. The lack of positive effect of soil Zn on plant Zn concentration, may have been caused by high positive correlation of soil Zn and soil Cd ($R = 0.85$, p-value < 0.001). In soils with low Cd concentration, there was a linear increase in plant Zn with increasing soil Zn, but the effect was reduced at higher concentration of Cd in the soil (data not shown). The negative effect of soil Cd on Zn uptake by plants is previously reported and maintained to be caused by antagonism in their uptake mechanism by plants [3, 21].

No satisfactorily consistent explanation of plant Cu either by Cu concentration in soil or from other soil properties in this study could be provided (R^2% for different models was between 38 and 52%). Significant positive relationship of plant Cu with soil Cu and Fe, and negative relationship with soil Cd, Mg, Mn, Zn, and soil pH was observed. Although, not a single model was suitable to explain Cu concentration in various plants.

None of the models used was found suitable to explain Co concentration in grass, however, the models explained its concentration in wheat grain, wheat straw, and maize better. In all the three models used for this plant type, soil pH negatively affected Co concentration in plants (Table 4). In addition, some negative effects of soil Cd, Mn and total C, and positive effect of soil Co and soil Cu, on plant Co were found. Except soil pH, none of the other soil factors showed consistent explanation for Co concentration in different plant species. As shown in Table 4, wheat grain Co and Mn were explained better by the same model. It was reported previously that Co is mainly found in the ferromagnesian minerals in the parent material and that Co cycle resembles very much to that of Mn [3], because Co and Mn having similar chemical properties are readily adsorbed by Mn oxides, and that Co availability is greatly influenced by Mn oxides activity and soil reactions which affect Mn [30].

Table 1. Mineral concentrations in soils of Kosovo in relation to their concentration worldwide (n = 73, concentrations given on DM basis)

Minerals	**Ranges**	**Mean ± SEM**	**Median**	**Worldwide average**[1]	**Common ranges in soil**[1]
Se, µg kg^{-1}	110–500	270 ± 9	280	330	5–3500
Zn, mg kg^{-1}	32–1400	96 ± 18	80	70	17–125
Cu, mg kg^{-1}	14–78	28 ± 1	24	38.9	1–205
Co, mg kg^{-1}	8–64	23 ± 1	20	8	0.5–70
Mo, mg kg^{-1}	0.4–3.2	1.3 ± 0.1	1.2	1.1	0.013–17
Mn, mg kg^{-1}	200–3100	1072 ± 63	1000	490	410–550
Fe, g kg^{-1}	12–53	30 ± 1	31	35	7–55
Cd, mg kg^{-1}	0.07–5.6	0.30 ± 0.07	0.23	0.41	0.01–2.5
Pb, mg kg^{-1}	16–2200	78 ± 30	43	32	3–189
Mg, g kg^{-1}	0.6–21.0	4.4 ± 0.4	3.0	-	-
P, g kg^{-1}	0.17–0.91	0.50 ± 0.02	0.49	-	-
S, g kg^{-1}	0.12–0.83	0.30 ± 0.02	0.27	-	-
C, %	0.7–5.0	2.2 ± 0.1	2.0	-	-
N, %	0.04–0.48	0.21 ± 0.01	0.19	-	-
C:N	8.5–19.1	11.3 ± 0.2	10.8	-	-
pH	4.7–7.9	6.5 ± 0.1	6.6	-	-

[1]Worldwide averages and common ranges in soil are based on a table provided by Kabata-Pendias (2011).

Table 2. Mineral concentrations in all selected plants (n = 73, concentrations given on DM basis)

Minerals	**Ranges**	**Mean ± SEM**	**Median**	**Requirements for animals**[1]	**Deficiency**	**Toxicity**
Se, µg kg^{-1}	5–97	16 ± 2	10	100–300	< 50	> 2000
Zn, mg kg^{-1}	2.3–116	31 ± 2	31	20–73	< 10–20	> 400
Cu, mg kg^{-1}	1.4–12.3	6.2 ± 0.3	5.9	7–18	< 4	> 20 (15)[2]
Co, mg kg^{-1}	0.01–1.07	0.1 ± 0.02	0.05	0.1–0.2	< 0.08	> 60
Mo, mg kg^{-1}	0.02–2.60	0.56 ± 0.06	0.48	> 0.5	< 0.2	> 135
Mn, mg kg^{-1}	10–460	68 ± 7	44	20–40	< 15	> 400
Fe, mg kg^{-1}	14–560	112 ± 12	68	30–50	> 30	> 300
Cd, mg kg^{-1}	0.01–1.1	0.08 ± 0.01	0.05	NA	NA	> 10(1)[3]
Pb, mg kg^{-1}	0.03–0.83	0.14 ± 0.01	0.1	NA	NA	> 100
Mg, g kg^{-1}	0.5–6.8	2.0 ± 0.1	1.6	0.8–2.9		
P, g kg^{-1}	0.2–6.4	2.8 ± 0.2	3.1	0.5–4.5		
S, g kg^{-1}	0.5–5.4	2.1 ± 0.1	1.7	1.4–2.6		

[1]Requirements, deficiency and MLT levels for animals are based on the literature (McDowell, 2003; NRC, 2005, 2007);
[2]Assuming normal concentrations of molybdenum (1–2 mg/kg diet) and sulfur (0.15–0.25%). At molybdenum and sulfur concentrations below these, copper may become toxic at lower levels;
[3]Cadmium MTL in brackets represents the upper limit in complete feed for animals used for human consumption set by WHO/IPCS (1992).

Table 3. Differences on mineral concentrations among plant species (concentrations given on DM basis)

Minerals	Grass (n = 27)		Maize (n = 24)		Wheat (n = 22)			
					Grain		Straw	
	Mean ± SEM	Median	Mean ± SEM	Median	Mean ± SEM	Median	Mean ± SEM	Median
Se, μg kg^{-1}	30 ± 4^{a}	27	11 ± 1^{b}	8	14 ± 3^{b}	8	9 ± 2^{b}	6
Zn, mg kg^{-1}	32 ± 2^{b}	29	46 ± 4^{a}	44	34 ± 2^{b}	33	11 ± 3^{c}	7
Cu, mg kg^{-1}	8.3 ± 0.4^{a}	8.5	8.7 ± 0.5^{a}	8.2	4.9 ± 0.2^{b}	4.8	2.2 ± 0.1^{c}	2.1
Co, mg kg^{-1}	0.15 ± 0.03	0.11	0.12 ± 0.04	0.07	0.05 ± 0.02	0.01	0.05 ± 0.02	0.02
Mo, mg kg^{-1}	0.93 ±0.14^{a}	0.61	0.39 ± 0.07^{b}	0.24	0.41 ± 0.07^{b}	0.36	0.44 ± 0.09^{b}	0.28
Mn, mg kg^{-1}	103 ± 22^{a}	60	78 ± 10^{ab}	72	36 ± 2^{b}	35	46 ± 8^{b}	33
Fe, mg kg^{-1}	200 ± 25^{a}	150	146 ± 23^{a}	95	39 ± 1^{b}	38	40 ± 11^{b}	26
Cd, mg kg^{-1}	0.04 ± 0.008	0.03	0.13 ± 0.02	0.1	0.05 ± 0.02	0.02	0.12 ± 0.05	0.05
Pb, mg kg^{-1}	0.19 ± 0.02	0.18	0.13 ± 0.02	0.09	0.11 ± 0.02	0.08	0.14 ± 0.04	0.06
Mg, g kg^{-1}	2.4 ± 0.2^{b}	2.4	3.4 ± 0.3^{a}	3.3	1.2 ± 0.0^{c}	1.2	0.9 ± 0.1^{c}	0.9
P, g kg^{-1}	3.4 ± 0.3^{a}	3.5	3.4 ± 0.2^{a}	3.0	3.8 ± 0.1^{a}	3.8	0.6 ± 0.1^{b}	0.5
S, g kg^{-1}	3.4 ± 0.2^{a}	3.2	1.8 ± 0.1^{b}	1.8	1.5 ± 0.0^{b}	1.5	1.4 ± 0.2^{b}	1.2

$^{a–c}$ Values with different superscripts significantly differ ($p < 0.05$).

Table 4. Regression models and the best predicting soil factors for micro mineral concentration in plants

Minerals in plant species		Intercept	Soil factors															R^2 (%)
			Cd	Co	Cu	Fe	Mg	Mn	Mo	P	Pb	S	Se	Zn	C	N	pH	
Se	G	0.002^{ns}	−0.069**	-	-	-	-	-	-	-	-	-	0.162***	-	-	-	-	45
	WG	0.015^{ns}	-	-	-	−0.001**	0.006***	-	-	-	-	−0.088***	0.141***	-	-	-	-	76
	WS	0.002^{ns}	-	-	-	-	0.002***	−0.011***	0.011**	-	-	−0.063***	0.057**	-	-	-	-	76
	M	0.012**	-	-	-	-	0.001***	-	-	-	-	−0.046***	0.017.	-	-	-	-	73
Zn	G	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	WG	19.13***	−23.05**	-	0.331**	-	-	-	4.530*	-	-	-	-	-	-	21.66*	-	64
	WS	3.950*	-	-	-	-	-	−2.458*	3.141*	-	-	9.673 .	-	-	-	-	-	41
	M	74.36**	-	-	1.589***	-	-	-	-	−44.14*	-	-	-	-	-	-	−7.411	46
Co	G	-	-	-	-	-	-	-	-	-		-	-	-	-	-	-	-
	WG	0.340**	−0.309*	-	0.005**	-	-	-	-	-	-	-	-	-	-	-	−0.054**	77
	WS	0.570***	-	-	-	-	-	-	-	-	-	-	-	-	−0.045*	-	−0.066**	47
	M	0.684*	-	0.017*	-	-	-	−0.306**	-	-	-	-	-		-	-	−0.095*	45
Cu	G	8.356***	-	−0.103	-	0.291**	−0.479*	-	-	-	-	-	-	−51.69*	-	-	-	37
	WG	0.340**	−0.309*	-	0.005**	-	-	-	-	-	-	-	-	-	-	-	−0.054**	52
	WS	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	M	12.83**	-	0.194*	-	-	-	−3.127*	-	-	-	-	-	-	-	-	−0.802 .	38
Mo	G	−5.800***	-	-	-	-	-	−0.436*	-	-	-	-	4.528***	-	-	-	0.918***	61
	WG	$−0.579^{ns}$	2.566**	-	0.014*	-	-	-	-	-	-0.007*	-	-	−13.51**	-	-	0.217**	70
	WS	−1.749***	-	-	-	-	-	−0.357**	-	1.285***	-	-	-	-	-	-	0.294***	75
	M	−1.509***	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.288***	55
Mn	G	1114***	-	-	4.062*	-	−14.71*	-	-	-	1.549*	−389.6**	-	-	-	-	−159.8***	71
	WG	77.06***	-32.40*	-	0.703**	-	-	-	-	-	-	-	-	-	-	-	−8.024**	52
	WS	410.6***	-	-	2.194***	-	−7.837***	-	25.45**	-	−0.717**	-	-	-	−17.09**	-	−51.31***	92
	M	359.3***	-	-	-	-	-	-	-	-	-	−193.4*	-	-	-	-	−35.99***	57
Fe	G	112.1^{ns}	590.2*	-	-	-	-	-	-	-276.7*	-	-	-	-	-	453.2	-	37
	WG	21.95***	-	-	0.661***	-	−1.410**	-	-	-	-	120.5***	-	-	−13.71**	-	-	71
	WS	158.7**	-	-	−3.763***	-	−10.25*	-	-	-	-	−192.2*	-	3080***	-	-	−25.00*	83
	M	112.6^{ns}	-	8.218*	-	-	-	−182.5**	-	-	3.657**	2552**	-	-	-	−396.8*	-	58
Cd	G	0.301***	-	-	0.003***	-	-	-	-	−0.093***	-	-	-	-	-	-	−0.045***	60
	WG	0.144***	-	-	0.001*	-	-	-	−0.014*	-	-	0.079*	-	-	-	-	−0.022***	69
	WS	0.412***	-	-	0.003**	-	−0.009**	-	-	-	−0.001*	0.165*.	-	-	-	-	−0.059***	78
	M	0.465**	0.529*	-	-	-	-	-	-	-	-	-	-	-	-	-	−0.068**	46
Pb	G	0.304***	0.771***	-	-	−0.005*	-	-	-	−0.293*	-	-	-	-	-	-	-	40
	WG	0.305*	-	-	-	-	-	-	-	−0.311***	-	0.923***	-	-	-	-	−0.046*	56
	WS	1.017***	-	-	-	-	−0.021*	-	-	-	-	−0.446*	-	2.994**	−0.0593	-	−0.126***	78
	M	0.472**	-	0.012***	-	-	-	−0.224***	-	-	-	-	-	1.583*	-	-	−0.071***	66

Values in the table are coefficients obtained by stepwise linear regression analysis for each particular soil factor; (*, **, ***) – express level of significance: < 0.05, < 0.01, and < 0.001, respectively; R^2 values stand for the regression model and not for a particular factor in the model; G = grass, WG = wheat grain, WS = wheat straw, M = maize.

Although a linear relationship between Mo content of herbage and its total concentration in soil is reported in the literature [3], it was not found in the present study. Molybdenum concentration in all plant species was positively affected by soil pH in (Table 4). Such relationship was reported earlier by [3], where Mo was found more mobile in alkaline soils. In addition, plant Mo showed some positive relationship with soil Cd, Cu, P, and Se, and negative relationship with soil Mn, Pb, and Zn. The positive effect of soil Cd on wheat grain Mo is rather unexpected because Mo mobility is higher in alkaline soils, while Cd mobility is higher in acidic soils [31, 32].

There was no linear correlation between soil and plant Mn concentration observed in this study. Regression analysis showed significant negative effect of soil pH on concentration of Mn in all plant species (Table 4). In addition, significant positive effect of soil Cu, and negative effect of soil Cd, Mg, S, and total C was also observed in the models, but these effects were not consistent for different plant types. This suggests that the main soil factor affecting plant Mn concentration was soil pH, as reported earlier in the literature [3].

No relationship between soil and plant Fe concentration was observed in this study (Table 4). Models predicting plant Fe were very complex and different for different plant species. The antagonistic relationship between plant Fe and soil Cd, Mn, Co, Cu, P, Zn have been reported in the literature [33]. However, in this study we observed such relationships only between plant Fe concentration and soil Mg (in wheat grain and straw); soil Mn (in maize); soil total C (in wheat grain); and soil pH (in wheat straw). In addition, there was a positive relationship of Fe in wheat grain with soil Cu and S, and negative relationship with soil Mg and soil total C (Table 4).

Linear correlation between soil and plant Cd was observed only in maize plants. Soil pH was the main factor affecting plant Cd, and it negatively affected plant Cd in all plant species analyzed. Soil pH alone explained up to 51% of plant Cd variation. Previously it was reported that Cd sorption is increased 3 times for each pH unit increase, and thus it has higher mobility in acidic soil [32, 33]. Other soil factors such as soil Mg and Pb (in wheat straw), soil P (in grass) and soil Mo (in wheat grain) were also negatively related with plant Cd. On the contrary, plant Cd was positively related with soil Cu (grass; wheat grain and straw) and S (wheat grain and straw).

No relationship between plant and soil Pb was observed in this study. Lead concentration in plants was negatively related with soil pH, and it was the main factor affecting plant Pb. In addition, plant Pb had negative relationship with soil Fe, Mg, Mn, P, and total C. On the contrary, soil Co and Zn had negative relationship with plant Pb.

Conflicts of Interest

No potential conflict of interest was reported by the authors.

Author Contributions

Methodology: AA; Formal analysis: AA; Investigation: AA, AB, HB; Resources: BRS; Writing – original draft: AA; Writing – review and editing: BRS, AB, HB; Supervision: BRS, AB; Project administration: BRS. All authors have read and agreed to the published version of the manuscript.

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References

[1] E. A. H. Pilon-Smits, C. F. Quinn, W. Tapken, *et al.*, “Physiological functions of beneficial elements,” *Curr. Opin. Plant. Biol.*, vol. 12, no. 3, pp. 267–274, 2009.

[2] F. M. Fordyce, “Selenium deficiency and toxicity in the environment,” in *Essentials of Medical Geology: Revised Edition*, O. Selinus, B. Alloway, J. A. Centeno, *et al.*, Eds., Dordrecht: Springer, 2013, pp. 375–416.

[3] A. Kabata-Pendias, *Trace Elements in Soils and Plants*, 4th ed., Boca Raton, FL: CRC Press; Taylor & Francis Group, 2011.

[4] M. Manojlovic and B. R. Singh, “Trace elements in soils and food chains of the Balkan region,” *Acta Agriculture Scandinavica, Section B—Soil & Plant Science*, vol. 62, no. 8, pp. 673–695, 2012.

[5] A. Ademi, A. Bernhoft, E. Govasmark, *et al.*, “Selenium and other mineral concentrations in feed and sheep’s blood in Kosovo,” *Translational Animal Science*, vol. 1, no. 1, pp. 97–107, 2017.

[6] A. Ademi, E. Govasmark, A. Bernhoft, *et al.*, “Status of selenium in sheep and dairy cow blood in Western Balkan countries,” *Acta Agriculture Scandinavica, Section A—Animal Science*, vol. 65, no. 1, pp. 9–16, 2015.

[7] P. E. V. Charman and B. W. Murphy, *Soils: Their Properties and Management*, South Melbourne, Australia: Oxford University Press, 2000.

[8] K. T. Osman, *Soils: Principles, Properties and Management*, Dordrecht: Springer Netherlands, 2013.

[9] H. P. Blume, G. V. Brümmer, H. Fleige, *et al.*, *Scheffer/Schachtschabel Soil Science*, Berlin, Heidelberg: Springer, 2016, ch. 5, pp. 123–174.

[10] Kosovo Environmental Protection Agency. (2015). Report on the state of water 2015. Prishtine: Ministry of Environment and Spatial Planning, Kosovo Environmental Protection Agency. [Online]. Available: http://www.ammkrks.net/repository/docs/Raporti_i_ujrave_i_2015__Anglisht.pdf

[11] Hydrometeorological Institute of Kosovo. (2018). Hidrometeorological yearbook of Kosovo 2015–2016. Prishtine: Ministry of Environment and Spatial Planning, Environmental Protection Agency of Kosovo, Hydrometeorological Institute of Kosovo. [Online]. Available: http://www.ammk-rks.net/repository/docs/Vjetari_2015-2016-EN7918.pdf

[12] Kosovo Agency of Statistics. (2018). Agricultural Holdings Survey 2017. Prishtine: Kosovo Agency of Statistics. [Online]. Available: http://ask.rks-gov.net/media/4319/agricultural-holdings-survey-2017.pdf

[13] D. W. Nelson and L. E. Sommers, “Total carbon, organic carbon, and organic matter,” in *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties*, A. L. Page, Ed., Madison, WI: American Society of Agronomy, Soil Science Society of America, 1982, pp. 539–579.

[14] J. M. Bremner and C. S. Mulvaney, “Nitrogen-Total,” in *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties*, A. L. Page, Ed., Madison, WI: American Society of Agronomy, Soil Science Society of America, 1982, pp. 595–624.

[15] J. Vejnovic, B. Djuric, P. Lombnæs, *et al.*, “Concentration of trace and major elements in natural grasslands of Bosnia and Herzegovina in relation to soil properties and plant species,” *Acta Agriculture Scandinavica, Section B—Soil & Plant Science*, vol. 68, no. 3, pp. 243–254, 2018.

[16] N. Terry, A. M. Zayed, M. P. De Souza, *et al.*, “Selenium in higher plants,” *Annu. Rev. Plant. Physiol. Plant. Mol. Biol.*, vol. 51, pp. 401–432, 2000.

[17] M. P. Rayman, "Selenium and human health," *Lancet*, vol. 379, pp. 1256–1268, 2012.
[18] H. F. Mayland, L. F. James, and J. L. Sonderegger, "Selenium in seleniferous environment," in *Selenium in Agriculture and the Environment*, L. V. Jacobs, Ed., Madison, WI: American Society of Agronomy, Soil Science Society of America, 1989, pp. 15–50.
[19] L. R. McDowell, *Minerals in Animal and Human Nutrition*, 2nd ed., Amsterdam, The Netherlands: Elsevier, 2003, pp. 283–311.
[20] N. F. Suttle, *Mineral Nutrition in Livestock*, 4th ed., Wellingford, UK: CAB Int., 2010.
[21] I. Cakmak, "Enrichment of cereal grains with zinc: Agronomic or genetic biofortification?" *Plant and Soil*, vol. 302, pp. 1–17, 2008.
[22] B. Lonnerdal, "Dietary factors influencing zinc absorption," *The Journal of Nutrition*, vol. 130, pp. 1378s–1383s, 2000.
[23] H. W. Lopez, F. Leenhardt, C. Coudray, *et al.*, "Minerals and phytic acid interactions: Is it a real problem for human nutrition?" *Int. J. Food Sci. Technol.*, vol. 37, no. 7, pp. 727–739, 2002.
[24] P. Schlegel, Y. Nys, and C. Jondreville, "Zinc availability and digestive zinc solubility in piglets and broilers fed diets varying in their phytate contents, phytase activity and supplemented zinc source," *Animal*, vol. 4, no. 2, pp. 200–209, 2009.
[25] National Research Council, *Mineral Tolerance of Animals*, 2nd rev. ed., Washington, D.C.: National Academies Press, 2005.
[26] M. E. Hodson and E. Donner, "Managing adverse soil chemical environments," in *Soil Conditions and Plant Growth*, P. J. Gregory and S. Nortclif, Eds., Hoboken, N.J.: Wiley-Blackwell, 2013.
[27] H. F. Li, S. P. McGrath, and F. J. Zhao, "Selenium uptake, translocation and speciation in wheat supplied with selenate or selenite," *New Phytol.*, vol. 178, no. 1, pp. 92–102, 2008.
[28] E. A. H. Pilon-Smits, G. S. Bañuelos, and D. R. Parker, "Uptake, metabolism, and volatilization of selenium by terrestrial plants," in *Salinity and Drainage in San Joaquin Valley, California: Science, Technology, and Policy*, A. C. Chang and D. B. Silva, Eds., Dordrecht: Springer Netherlands, 2014, pp. 147–164.
[29] N. C. Uren, "Cobalt and manganese," in *Heavy Metals in Soils: Trace Metals and Metalloids in Soils and Their Bioavailability*, B. J. Alloway, Ed., Dordrecht: Springer Netherlands, 2013, pp. 335–366.
[30] C. C. Johnson, X. Ge, K. A. Green, *et al.*, "Selenium distribution in the local environment of selected villages of the Keshan Disease belt, Zhangjiakou District, Hebei Province, People's Republic of China," *Appl. Geochem.*, vol. 15, no. 3, pp. 385–401, 2000.
[31] T. H. Christensen, "Cadmium soil sorption at low concentrations: I. Effect of time, cadmium load, pH, and calcium," *Water, Air, and Soil Pollution*, vol. 21, no. 1, pp. 105–114, 1984.
[32] E. Smolders and J. Mertens, "Cadmium," in Heavy Metals in *Soils: Trace Metals and Metalloids in Soils and their Bioavailability*, B. J. Alloway, Ed., Dordrecht: Springer Netherlands, 2013, pp. 283–311.
[33] J. L. Havlin, S. L. Tisdale, L. N. Werner, *et al.*, *Soil Fertility and Fertilizers: An Introduction to Nutrient Management*, 7th ed., Upper Saddle River, N.J.: Pearson Prentice Hall, 2005.