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Original Scientific paper

CORRELATION BETWEEN THE CONTENT OF HEAVY METALS IN SOIL AND TOBACCO FROM SOME MUNICIPALITIES OF SKOPJE PRODUCTION REGION

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ABSTRACT

The purpose of this research was to determine the correlation between content of Pb, Cd, Zn, Cu, Mn and Fe in soil and tobacco leaves from production regions from Skopje. 39 soil samples and 117 leaves were taken for carrying out this research. Some tested soils have Mn and Fe content above the permitted limits that is probably result of the secondary pollution (traffic and industry). Lead, cadmium, manganese and iron content in tobacco raw from several smaller production sites are above maximum allowable concentration, but are close to the obtained results by several researchers. According to correlation analyses, clay and humus have prominent influence on the content of the Pb, Cd, Cu and Zn in the soil, and weak correlation only with the lead and copper in the tobacco leaves. There is no significant correlation between the content of heavy metals in the soil and in tobacco leaves.

Keywords: soil, tobacco, heavy metals, lead, cadmium, copper, zinc, manganese, iron.

КОРЕЛАЦИЈА МЕЃУ СОДРЖИНАТА НА ТЕШКИ МЕТАЛИ ВО ПОЧВАТА И ТУТУНОТ ОД НЕКОИ ОПШТИНИ ОД СКОПСКИОТ ПРОИЗВОДЕН РЕГИОН

Целта на истражувањето беше да се утврди корелацијата помеѓу содржината на Pb, Cd, Zn, Cu, Mn и Fe во почвата и тутунските лисја од производствените региони од Скопје. 39 почвени примероци и 117 листови тутун беа земени за извршување на ова истражување. Неколку примероци од анализираните почви имаат содржина на Mn и Fe над дозволените граници што е веројатно резултат на секундарно загадување (сообраќај и индустрија). Содржината на олово, кадмиум, манган и железо во тутунската суровина од неколку помали производствени места се над МДК, но се блиску до добиените резултати од страна на неколку истражувачи. Според корелационата анализа, содржината на глина и хумус имаат влијание врз содржината на Pb, Cd, Cu и Zn во почвата и слаба корелација само со оловото и бакарот во тутунските лисја. Не постои значајна корелација помеѓу содржината на тешки метали во почвата и во лисјата тутун.

Клучни зборови: soil, tobacco, heavy metals, lead, cadmium, copper, zinc, manganese, iron.

INTRODUCTION

Today, as a result of modern civilization, the world is facing a serious problem of pollution by harmful substances which certainly include heavy metals. Pollution is particularly critical near: power stations, mines, along the roads, soil fed with fertilizers and pesticides, landfills with industrial and organic wastes, etc. (Pelivanoska, 2007). The intensive use of mineral fertilizers and plant protection products containing Cu and Zn in agricultural production distort the balance of heavy metals in soil, allowing it to penetrate through the chain of animal and human nutrition through plants, through drinking water or through nutrition of farm animals that feed on surfaces contaminated with heavy metals. Heavy metals in form of fine particles of dust can be found in the atmosphere from where they are deposited in soils and water as insoluble compounds of carbonates, sulfates or sulfides. Soil pollution by heavy metals is a serious problem for agricultural production as basis of food production. Heavy metals accumulate in the biomass of successive food consumers. At the end of the food chain using this biomass are people. Heavy metals toxicity for living organisms and humans depends on their quantity for each item that is different and vary in wide range. Tobacco is widespread crop that is produced on every continent of the globe. Because of the specificity of its use, tobacco is treated as food product. Therefore, tobacco is subjected to stringent global criteria in terms of maximum concentration of certain heavy metals such as: Pb, Cd, Cu, Zn, Mn, Fe and others. There are 16 hot spots of contamination identified in Macedonia. Skopje is the capital and largest city in the country, and also an administrative political, economic, cultural, scientific and educational center. The industrial part of the city of Skopje is located on the southeast and east part where most of the tobacco production is placed.

Given that there are several industrial facilities in the Skopje production region that may pollute the soil, water and agricultural plants, our main goal was to determine the content of heavy metals in the tobacco raw produced in this region. Based on the obtained results we can conclude whether oriental tobacco grown in this region, despite its high quality and aroma represents environmentally safe raw material for both domestic and foreign market.

MATERIAL AND METHOD

Sampling locations

Studies were performed in 2008 in Skopje tobacco producing area. Soil and raw tobacco samples were taken from 11 settlements (Table 1). In most of the sampled places, oriental tobacco type Prilep and Yaka are produced. Only small areas produce semi- oriental tobacco type Otlia. Studies were performed of tobacco type Prilep which in this area represents over 97 %. There are 9 municipalities in Skopje production area: Studeničani, Butel, Zelenikovo, Petrovec, Gazi Baba, Aračinovo, Kisela Voda, Aerodrom and Čučer Sandevo. In the industrial part of the municipality Kisela Voda are located several large facilities in the chemical and metal industry (such as „Ohis“, „Tulana“ previous „Tipo“, newly opened factory for steel constructions „Prototip Stil“), glass factory, services and workshops etc. In the vicinity of the organic-chemical industry "Ohis" as one of the biggest polluters is located the cement factory "Usje" now "Titan", that performs excavation in municipalities of Dračevo and Studenicani. Also in this area, the textile factory "Hemteks" was located. The functioning of these industries is a hotspot for potentially environmental pollution in this tobacco producing area.

Soil analysis

39 composite soil samples were collected from the upper layer (0-30 cm) of each field with two replicates. At the same sites where soils were sampled, tobacco leaves with two replicates from three picking belt were collected. First picking belt included lower leaves, second middle and third picking belt, upper leaves. Samples were taken from Skopje municipalities given in Table 1. Preparation of soil samples was performed in accordance with ISO 11464:2006. Soil samples first were air-dried, after that crushed and sieved through a 2-mm sieve. Physical properties such as clay content (Resulovič H. 1971), pH (ISO 10390:2005), total nitrogen (ISO 11361:1995), humus (Tjurin, 1931, validated at the Scientific Tobacco Institute - Prilep, Macedonia), available phosphorus and potassium (*Džamić*, 1996, AL method, validated at the Scientific Tobacco Institute - Prilep, Macedonia) were measured. Concentration of metals was determined using the Aqua Regia ($HCl-HNO_3$, 3:1) extraction method (ISO 11466:1995) after digestion at 180ºC for 2 h. All reagents were of analytical grade (Merck, Germany). Heavy metals were determined by flame atomic-absorption spectrophotometry (FAAS, ISO 11047:1998). Cadmium and lead were measured by graphite furnace atomic-absorption spectrophotometry (GFAAS).

Plant analysis

Oriental tobacco leaves were washed to remove any adhering soil particles and rinsed with distilled water. After that, leaf samples were placed in paper bags, dried at 75 ^{o}C for 12 hours and ground using a mortar and pestle. Appropriate blanks were included in all extractions. Samples are mixture from three priming belts from each sample point. Heavy metals were determined by flame atomic-absorption spectrophotometry (FAAS, ISO 11047:1998). Cadmium and lead were measured by graphite furnace atomic-absorption spectrophotometry (GFAAS).

Statistical analysis

The data were statistically analyzed using correlation analysis (Pearson correlation, two-tailed). Results from two replicates were averaged prior to statistical analyses. Correlation analysis was used to establish relationships between physical and chemical characteristics of the soil samples, and between such characteristics and the heavy metal content of oriental tobacco leaf samples from three parts of the plant. Statistical analyses were performed with the aid of SPSS 9.0.

RESULTS AND DISCUSSION

Soil analyses

Agrochemical analyses of soils samples are given in Table 1. According to obtained data from agrochemical analysis, soil samples contain larger quantity of physical clay. Clayey soils are represented with 64.10 %, and loamy with 35.90 %. According to classification these soils are cambisols, very suitable for tobacco production. Only two samples had physical clay of over 80 % and it is advisable that they are omitted for production of the tobacco. High quality oriental type tobacco usually grows in soils with lower organic matter content. It is believed that the optimum content of humus in the soil for production of oriental tobacco is 1-1.5 % (Patće and Uzunoski 1966).

Soils that contain small amounts of nitrogen are also suitable for production of the oriental tobacco types. According to Georgieski (1957), the most adequate soils are the ones where total nitrogen content is from 0.08 % to 0.09 %. From our results, most of the samples had low to moderate content of nitrogen, and are very suitable for tobacco production.

Table 1. Agrochemical parameters of soils from the sampling locations from Skopje production region

Sampling location	Humus %	Total nitrogen %	pH		$CaCO_3$ %	mg/100 g soil		Clay <0,02 mm %	Texture soil classification according to Vigner
			H_2O	KCl		P_2O_5	K_2O		
Studeničani	1.02	0.054	8.01	7.23	2.35	35.85	16.81	29.6	Light loam
Studeničani	0.88	0.046	7.95	7.15	2.69	22.12	20.84	39.8	Medium loam
Studeničani	1.07	0.076	7.51	6.76	0.67	7.88	24.87	49.4	Heavy loam
Studeničani	1.81	0.112	7.46	6.46	9.58	3.05	23.53	70.8	Medium clay
Studeničani	0.87	0.048	7.82	7.08	1.68	62.55	19.83	22.9	Light loam
Studeničani	1.10	0.058	7.79	7.08	1.26	70.94	17.81	23.2	Light loam
Studeničani	1.41	0.067	7.58	6.76	3.19	78.31	29.91	44.5	Heavy loam
Studeničani	0.77	0.039	7.66	6.83	1.01	72.21	22.18	31.5	Medium loam
Morani	0.82	0.043	7.49	6.74	0.0	69.41	19.16	29.9	Light loam
Morani	2.03	0.109	7.51	6.70	20.07	16.53	29.58	77.6	Heavy clay
Morani	1.90	0.062	7.49	6.68	4.79	23.14	24.87	61.5	Medium clay
Morani	1.74	0.086	7.52	6.68	12.03	12.46	20.84	59.8	Light clay
Orešani	1.72	0.092	5.36	4.52	0.0	9.15	30.92	64.1	Medium clay
Orešani	2.10	0.105	4.79	3.83	0.0	7.88	28.90	69.1	Medium clay
Vražale	1.75	0.102	7.14	6.30	19.65	10.68	17.48	67.6	Medium clay
Vražale	2.00	0.086	7.21	6.42	1.51	15.76	18.82	56.3	Light clay
Vražale	1.92	0.086	5.15	4.09	0.0	3.97	20.84	59.7	Light clay
Vražale	1.38	0.084	7.18	6.30	0.0	3.81	17.48	67.5	Medium clay
Vražale	2.51	0.104	5.42	4.46	0.0	6.87	26.22	62.5	Medium clay
Zelenikovo	1.68	0.074	5.34	4.32	0.0	7.37	25.54	63.6	Medium clay
Zelenikovo	2.22	0.094	7.23	6.45	0.0	68.40	62.51	71.3	Medium clay
Pakoševo	2.17	0.137	7.41	6.54	2.52	63.57	67.80	71.1	Medium clay
Strahojadica	1.26	0.049	6.50	5.48	0.0	6.61	24.00	37.0	Medium loam
Strahojadica	1.33	0.069	6.46	5.46	0.0	7.88	29.20	53.7	Light clay
Gumajlevo	1.72	0.101	7.41	6.50	9.24	13.48	33.80	61.9	Medium clay
Gumajlevo	1.73	0.070	7.54	6.78	6.22	63.06	24.60	39.4	Medium loam
Gumajlevo	1.68	0.101	7.26	6.49	2.52	38.65	68.40	70.9	Medium clay
Gumajlevo	3.66	0.187	7.22	6.48	10.59	200.36	107.40	73.4	Medium clay
Gumajlevo	1.05	0.065	7.29	6.45	6.47	20.09	31.90	57.2	Light clay
Smesnica	1.60	0.069	5.95	4.99	0.0	3.71	25.00	54.7	Light clay
Smesnica	1.71	0.092	5.69	4.71	0.0	5.34	30.60	42.1	Heavy loam
Smesnica	1.62	0.099	6.28	5.18	0.0	9.31	34.50	61.5	Medium clay
Smesnica	1.21	0.078	6.27	5.12	0.0	4.73	32.70	60.1	Medium clay
Smesnica	1.83	0.079	6.52	5.54	0.0	39.41	71.50	61.4	Medium clay
Smesnica	1.18	0.068	6.21	5.13	0.0	3.56	18.50	47.4	Heavy loam
Smesnica	1.49	0.087	7.49	6.63	0.76	10.17	30.60	49.3	Heavy loam
Dračevo	2.37	0.145	7.64	6.70	4.12	12.20	30.60	84.6	Heavy clay
Dračevo	1.65	0.108	7.83	6.83	5.38	23.90	35.20	85.1	Heavy clay
Dolno konjare	2.24	0.102	7.75	6.78	2.69	21.61	33.80	49.2	Heavy loam

Based on the results, most of the samples (69.23%) have low organic matter content, and with medium content are 28.20 % of the soil samples. According to these results, except one sample, all sampled soils are adequate for production of high quality oriental tobacco.

Table 2. Trace elements content in soil samples

Sampling place	Pb mg/kg	Cd mg/kg	Cu mg/kg	Zn mg/kg	Mn mg/kg	Fe mg/kg
Studeničani	14.11	0.367	12.40	45.05	588.7	7684.8
Studeničani	14.33	0.267	14.74	54.34	979.7	7533.2
Studeničani	20.78	0.367	17.38	70.77	1056.9	7776.0
Studeničani	20.11	0.400	20.54	75.95	690.8	7830.7
Studeničani	13.00	0.367	12.00	49.15	470.1	6906.3
Studeničani	14.11	0.367	11.88	73.73	705.2	6790.2
Studeničani	16.33	0.367	20.47	75.38	756.1	7657.3
Studeničani	13.78	0.333	13.38	52.64	505.7	7332.6
Morani	14.00	0.300	12.61	49.50	539.3	7083.0
Morani	15.44	0.367	23.70	74.07	1056.8	7758.8
Morani	17.78	0.400	21.77	75.78	1009.3	7791.3
Morani	15.67	0.333	19.94	68.24	896.5	7737.7
Orešani	22.67	0.333	27.74	83.61	1142.3	7785.3
Orešani	24.44	0.433	38.70	90.45	1072.5	7788.0
Vražale	16.00	0.333	22.90	81.31	978.2	7757.0
Vražale	20.67	0.367	20.83	81.89	1443.0	7799.2
Vražale	18.11	0.267	14.02	78.88	593.9	7828.1
Vražale	18.78	0.367	24.27	84.73	1744.4	7836.6
Vražale	19.11	0.300	16.33	72.65	382.2	7818.0
Zelenikovo	21.33	0.333	34.08	75.34	963.8	7715.0
Zelenikovo	21.11	0.433	37.38	102.03	919.7	7826.7
Pakoševo	22.78	0.333	31.57	92.55	1315.9	7748.1
Strahojadica	15.44	0.367	15.08	72.11	883.9	7780.1
Strahojadica	18.33	0.233	17.80	80.49	827.1	7793.5
Gumajlevo	17.67	0.367	24.00	94.53	931.1	7823.7
Gumajlevo	13.11	0.433	16.20	62.28	1354.4	7658.2
Gumajlevo	14.67	0.367	22.10	92.52	724.2	7828.0
Gumajlevo	22.00	0.367	28.90	111.70	946.1	7791.2
Gumajlevo	12.11	0.367	16.98	72.91	775.3	7752.3
Smesnica	17.00	0.200	17.10	76.01	664.4	7779.9
Smesnica	19.67	0.233	25.34	113.87	783.7	7851.1
Smesnica	20.33	0.333	20.13	92.88	691.4	7788.5
Smesnica	16.67	0.367	18.40	74.78	659.6	7801.7
Smesnica	19.44	0.300	17.77	82.25	631.5	7813.0
Smesnica	15.00	0.300	16.34	76.25	658.5	7801.7
Smesnica	18.33	0.267	17.28	73.65	763.0	7757.8
Dračevo	21.67	0.300	26.77	86.65	1080.3	7807.2
Dračevo	20.11	0.367	25.61	85.02	1027.9	7793.0
Dolno konjare	16.33	0.367	21.58	75.03	1080.9	7790.9

Soil pH is from 5.15 to 8.01 that is also favorable condition for production of high quality tobacco. Most of the samples are non-carbonate soils, (41.02%). 10.26% have high carbonate content of over 10 %. Most soil samples are well supplied with available phosphorus. Very high content of this parameter is found in 11 soil samples. In these areas it is good to avoid tobacco cultivation or to avoid phosphorus fertilization for many years.

Heavy metal content of soil samples is given in Table 2. Based on the results we can conclude that Pb, Zn, Cu and Cd content are bellow the allowable limits (Sluzbeni list RH NN 1/97), therefore they are suitable for tobacco and agriculture production. Part of the sampled soils has Mn and Fe content that is above allowable limits. This is probably due the secondary pollution from the industry and traffic. These sampling spots are mostly in the settlements Oreshani, Smesnica and Gumajlevo that are very small production areas. According to Jekić (1985) Mn content in soil is 200-400 mg/kg (0.02-0.04 %) as total manganese, usually in the form of inorganic reserves. The content of manganese in soil and its accumulation in soil horizons depends on subsoil, soil pH, redox potential, moisture, humus and microbial activity (Stojkoska, 1987). Pelivanoska (2011) in soils for tobacco production found Mn content from 56.03 to 3 143 mg/kg. Our data are consistent with presented literature data.

Iron as one of the most widespread elements of the earth's crust in the tested soils ranges between 6790.2 to 7851.1 mg/kg. Average value of Fe is 7697.32 mg/kg, which is similar as soils from Prilep and Kumanovo area (Mitrikeski, 2000).

Plant analyses

Descriptive statistics of metals content from the oriental tobacco leaves from Skopje producing region in given in Table 3. As we can see average Pb content is from 22.06 mg/kg in middle leaves, 22.01 mg/kg in upper leaves to 22.75 mg/kg in the lower leaves. Variation coefficients for the lower and middle leaves are similar and are around 14.37 %, and in upper leaves it is 20.26 %. Data from these studies are close to the literature data from Pelivanoska (2007) and Golia et al., (2001) but significantly higher than the maximum permissible concentrations (Zakon za bezbednost na hrana, Sl. Vesnik 54, 2004). Average Cd content of the examined tobacco leaves is 2.32 mg/kg. Minimum content of Cd is 0.55 mg/kg in the lower leaves, and maximum 7.6 mg/kg in the upper leaves. According to descriptive statistics and coefficient of variation, cadmium content of tobacco leaves has large variation. This indicates inhomogeneity, and only in small number of localities tobacco has higher than tolerant content cadmium of 3.0 mg/kg (Tso, 1990). Nadkarni (1974) points out that in tobacco we can found 1-2 mg/kg cadmium. Based on our findings, Cd content above permissible limits is detected in some samples from Oreshani, Vrazhale, Zelenikovo, Starhojadica and Smesnica (Tables 1, 2). The survey results show a local increase in the cadmium content that can be explained by the existence of a large number of sources of pollution in the vicinity of the studied sites of the Skopje production region.

Zinc and copper are important trace elements and play an important role in enzyme activity and are involved in the chlorophyll formation (Foy et al, 1978). In plants Zn content is 20-100 mg/kg (Pelivanoska, 2007), and Cu content is to 20 mg/kg (Kastori 1993). Zink deficiency in plants is detected in contents less than 20-25 mg/kg, and Zn toxicity is detected at 400 mg/kg (Jakovlević et al., 1991). Jekić (1985) points out that zinc toxicity occurs very rarely. Average Zn content in the tobacco leaves is from 15.79 to 66.34 mg/kg. Highest content is found in the lower leaves from 6.73 до 68.01 mg/kg Zn, with average of 39.39 mg/kg. Middle leaves have 11.77 to 76.97 mg/kg Zn, or average 39.04 mg/kg. Upper leaves have the smallest content of Zn (17.23-74.73 mg/kg), with average measured values of 38.15 mg/kg. Our data is close to the data of Grabuloski (1985) and Pelivanoska (2010).

The average copper content depending on its location on the tobacco plant is highest in the upper harvests (7.54 mg/kg), lower in lower harvests (7.08 mg/kg) and lowest in the middle harvests (6.88 mg/kg). Variation coefficient is 35.87%-37.8%. According to Pashoski (1980) plant tissue has 1.5-2.0 mg/kg Cu. If the content is less, signs of deficiency appear, and if copper content of dry matter of plants is 20-30 mg/kg, it can adversely affect the yield and quality of the tobacco. Tso (1990) points out Cu content in tobacco of 15-21 mg/kg. The content of zinc and copper in tobacco leaves is lower than permissible limits in all tested samples and there is no danger of their detrimental effect on the quality of tobacco raw.

Table 3. Descriptive statistics of metals content from the Oriental tobacco leaves from Skopje producing region in mg/kg

		Tobacco sampling belt			
Heavy metal	Statistical index	Lower leaves	Middle leaves	Upper leaves	Average
Pb, mg/kg	Average mg/kg	22.74	22.06	22.01	22.18
	Minimum, mg/kg	12.00	11.50	11.50	11.60
	Maximum, mg/kg	28.50	28.50	27.00	28.20
Cd, mg/kg	Average, mg/kg	2.32	2.06	1.94	2.09
	Minimum, mg/kg	0.55	0.70	0.70	0.67
	Maximum, mg/kg	6.70	4.95	7.60	5.83
	CV, %	71.12	64.08	86.60	69.99
Cu, mg/kg	Average, mg/kg	7.08	6.88	7.54	7.52
	Minimum, mg/kg	3.40	2.90	3.25	3.07
	Maximum, mg/kg	12.60	11.90	12.65	12.19
	CV, %	35.87	35.90	37.80	36.27
Zn, mg/kg	Average, mg/kg	39.39	39.04	38.15	38.86
	Minimum, mg/kg	6.73	11.77	17.23	11.91
	Maximum, mg/kg	68.01	76.97	74.73	73.23
	CV, %	40.77	40.96	45.90	36.49
Mn, mg/kg	Average, mg/kg	147.48	105.13	122.02	116.98
	Minimum, mg/kg	30.40	44.50	32.45	39.27
	Maximum, mg/kg	670.70	300.55	578.35	430.14
	CV, %	72.75	45.42	85.11	58.82
Fe, mg/kg	Average, mg/kg	1050.1	821.63	659.83	843.85
	Minimum, mg/kg	302.80	327.15	225.00	284.98
	Maximum, mg/kg	2232	2108.15	2096.55	2145.57
	CV, %	47.19	56.54	59.93	49.05

Referent values for Mn content in tobacco leaves are in broad boundaries from 140 to 700 mg/kg (Pelivanoska, 2007). The survey results showed that the content of manganese is within range of 30.40 mg/kg in Smesnica to 670.70 mg/kg in Vrazhale. Lower harvest leaves have highest manganese content. These values are similar to those obtained by Grabuloski et al. (1985). These authors found that Mn content is higher in the lower leaves, while equally distributed in middle and upper leaves. Toshev (1969) detected the same distribution. According to these authors, Mn content in lower leaves is 145 mg/kg and 100 mg/kg in upper leaves.

Average Fe content of the tobacco raw from Skopje production area is from 284.98 to 2145.57 mg/kg. The highest average content of iron is in a leaves from lower harvest (1050.10 mg/kg), and lowest in the upper leaves (659.83 mg/kg). There is high coefficient of variation from all harvest zones. There are high fluctuations from 47.19% in lower leaves, to 59.93% in upper leaves. Our results are similar to ones from Grabuloski et al. (1985) where Fe content is to 1314 mg/kg. Same authors present data from many researches (Nadkarni, 1974; Jones et al., 1991, Campbell, 2000) that found Fe content in tobacco raw that is from 292 to 572 mg/kg. Pelivanoska (2010) detected values from 22.45 to 438.30 mg/kg. Miceska (2005) also found 0,37 до 0,64 mg/g Fe dry matter of tobacco type Prilep.

Correlation analysis

The content of heavy metals in tobacco leaves is a variable and depends on the conditions in which tobacco is grown, and mostly of the soil composition and its properties (Zaprijanova, 2010). One of the main soil parameters that affect the heavy metals content in tobacco is soil pH (Xian and Shokonifard, 1989, King and Hajjar 1990, Khan et al., 1992, Bell et al., 1992). Golia et al. (2007) found significant negative correlation among soil pH and heavy metal content in oriental tobacco. These authors found no relationship between total content of metals in the soil and in the leaves of oriental tobacco.

Table 4. Correlation among soil parameters and heavy metal concentration in both, tobacco leaves and corresponsive soil samples

Parameter	Pb-S	Cd-S	Cu-S	Zn-S	Mn-S	Fe-S	Pb-L	Cd-L	Cu-L	Zn-L	Mn-L	Fe-L
Humus	**0.612**	0.143	**0.604**	**0.670**	0.276	**0.492**	*0.366*	0.121	*0.356*	0.229	0.176	0.044
pH	**-0.447**	0.301	-0.290	*-0.345*	0.141	*-0.352**	*-0.411*	**-0.720**	**-0.609**	**-0.459**	-0.195	-0.285
Clay	**0.636**	0.134	**0.697**	**0.633**	*0.384*	**0.688**	*0.382*	0.164	*0.406*	0.388	0.164	0.125
Pb-S	1.000	0.025	**0.750**	**0.663**	*0.369*	**0.496**	0.292	*0.381**	**0.564**	**0.450**	*0.347*	0.135
Cd-S		1.000	0.310	*0.011*	0.332	0.038	**0.080**	0.303	0.080	-1.134	0.152	-0.022
Cu-S			1.000	**0.695**	**0.497**	**0.460**	*0.380*	*0.360**	**0.567**	**0.410**	0.312	0.096
Zn-S				1.000	0.303	**0.545**	*0.376*	*0.366**	**0.417**	**0.377**	0.211	0.202
Mn-S					1.000	*0.332**	0.190	-0.115	0.304	0.160	*0.394*	0.036
Fe-S						1.000	0.106	0.311	**0.438**	**0.555**	0.196	**0.465**
Pb-L							1.000	0.279	**0.462**	0.170	0.265	0.174
Cd-L								1.000	**0.744**	**0.657**	0.248	0.224
Cu-L									1.000	**0.768**	**0.462**	0.246
Zn-L										1.000	0.150	**0.469**
Mn-L											1.000	**0.536**
Fe-L												1.000

Pb- S is for soil samples; Pb- L is for tobacco leaves; Bold coefficients represent that correlation is significant at $\alpha = 0.01$; Italic coefficients represent that correlation is significant at $\alpha = 0.05$.

Correlation coefficients of soil parameters and the content of heavy metals in soil and tobacco leaves from Skopje production area are presented in Table 4. Based on the results it can be seen that the content of organic matter (or humus) in soil has a strong correlation with the content of Pb, Cu, Zn and Fe in the soil, and no correlation with the content of Cd and Mn. The content of humus in the soil has no significant relation to the contents of Pb and Cu in raw tobacco. Soil pH has significant correlation with Pb, Zn and Fe content from soil, while in tobacco raw this soil parameter has a strong correlation at the level of 0.01 with Pb, Cd, Cu and Zn, and no correlation with Mn and Fe. This research confirms the findings of the previously mentioned literature data. Pelivanoska et al., (2011) did not find correlation among soil pH and heavy metals in tobacco leaves. Cu content in soil has strong correlation with other soil parameters such as organic matter and clay, with soil Zn, Mn and Fe content and Cu and Zn content in the tobacco. Weak correlation is found among Cu soil content and Pb and Cd content from the tobacco raw. The results of the analysis indicate that the copper content in soil affects the copper content in tobacco leaves. Overall we can conclude that from all examined soil parameters as independent variables, soil pH showed the greatest influence on the content of the Pb, Cd, Cu and Zn, while it shows no influence on the content of Mn and Fe.

The clay and humus have significant influence on the content of the studied elements in the soil, and only weak correlations with lead and copper in tobacco raw.

CONCLUSIONS

According to agrochemical analysis of soils from Skopje production area, we can conclude that they are suitable for tobacco production. Only few soils samples make exception and are less convenient and these are soils where it is difficult to ensure the production of quality tobacco raw.

Pb, Cd, Cu and Zn content in soils are in allowable limits and these soils are suitable for production of tobacco as well as other crops. Part of the sampled soils have Mn and Fe content above reference values that might be result of natural background or pollution of air, industry and traffic. These samples are from Oreshani, Smesnica and Gumajlevo where tobacco production is low.

Results show geographical trends in lead and cadmium content with values above reference limits that can be explained by many sources of pollution in Skopje production area. Zn and Cu content in tobacco leaves are above the reference values, Mn is in the allowable limits and Fe content is above reference values only in few samples.

Soil pH has the most significant influence on the content of Pb, Cd, Cu and Zn, while no influence on the content of Mn and Fe. Clay and humus has most prominent influence on the content of heavy metals in soil samples, and less significant correlation only with lead and copper content in tobacco raw.

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