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ASSESSMENT OF THE CONTENT OF CHEMICAL ELEMENTS IN SOIL AND ITS PROPERTIES USED FOR TOBACCO CULTIVATION IN THE REPUBLIC OF MACEDONIA

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Abstract

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The objectives of the presented study were to assess the properties of soil from different agricultural areas in the Republic of Macedonia used for tobacco cultivation determining the most important soil factors (pH, clay, cation exchange capacity - CEC, organic matters - OM and total organic carbon - TOC) that influence the content of metals in soil. The study was conducted on 150 locations from three well-known tobacco regions in Macedonia (Pelagonia, Southeastern region and Vardar Valley). Total (HF digestion) and pseudo-total (aqua regia extraction) content of eighteen elements (Ag, Al, Ba, Ca, Cr, Cu, Li, Fe, K, Mg, Mn, Na, Ni, Pb, P, V, Sr, and Zn) was analyzed by atomic emission spectrometry with inductively coupled plasma (ICP-AES). The results suggested the general effectiveness of total digestion for determination of most of the elements. Aqua regia extraction was more successive for the extraction of Cu, Pb, Zn and P. Significant positive correlations were found between clay, CEC and total content as well as aqua regia extractable elements content. Organic matters had significant positive correlation with most of the pseudo-total elements, and positive significant correlation only with the total content of Ba, Li and P. All analyzed element correlated poorly with pH, total organic carbon (TOC) and had high inter-element correlation. Despite intensive tobacco production, the content of most of the heavy metals in soil were at levels, which are typical of agricultural and low anthropogenic pressure areas. However, some plots had high Ni content. Based on the results of all investigated variables and giving the importance of tobacco production for Macedonian, further and extended monitoring is crucial.

Key words: Agriculture, Trace Elements, Tobacco, Soil Properties

Abbreviations: PR - Pelagonia region; SER – South-eastern region; VV - Vardar Valley; CEC - Cation exchange capacity; OM- Organic matter; EC – Electroconductivity; TOC - Total organic carbon; AR - Aqua regia extraction method (ISO 11466); HF - Total HF digestion method (ISO 14869-1:2001)

Introduction

Soil is the fundamental base of agricultural production and extremely important multifunctional medium for crop growth, crop productivity and maintaining the environmental quality. Beside all simultaneous and vital functions, this resource is not immune to the disturbance of the ecological balance, thus monitoring of soil properties is essential to achieving sustainable land use.

Contamination with trace elements and their accumulation in agricultural production systems is potential threat affecting food quality, crop growth and directly affecting the environmental health (McLaughlin at al., 2000; Micó et al., 2006; Peris at el., 2007). Agricultural soils act as good sinks

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where trace elements and other pollutants accumulate rapidly but their depletion is very slow. Although metals occur naturally (Fadigas et al., 2010; Kabata-Pendias, 2011), agricultural soils are affected by anthropogenic influence mainly with application of sludge, manure, pesticides, inorganic fertilizers and waste water application (Drury et al., 2009; Sheppard et al., 2009). The use of phosphate fertilizers is basic factor of pollution, containing high concentration of heavy metals (Golia et al. 2009; Kabata and Pendias, 2011). Numbers of factors contribute to the mobility and availability of those elements such as bioecological characteristics of plant species, concentration and chemical forms of appearance of elements in soil and certainly eco-pedological conditions (Alloway, 1999; Kabata-Pendias, 2011).

Republic of Macedonia is widely known for its high quality oriental tobaccos and it produces 3% of the total oriental tobacco in the world (Kabranova and Arsov, 2009). About 90% of the total tobacco produced is exported and this culture is a strategic product viewed from economic, trade, fiscal, social and demographic aspects. One of the objectives of this research was to conduct a survey based on the heavy metal content required for monitoring future pollution trends in agricultural soils used for tobacco cultivation. Due the fact that tobacco has a large use in the cigarette industry and is one of the crops with increased uptake and accumulation of heavy metals (Golia et. al., 2001; Metsi et al., 2001; Zaprijanova et al., 2010) it is very important regarding human health, for continuous investigation and assessment of the level of these elements both in soil and tobacco raw. Despite the importance of this crop, there is limited information available on levels of trace elements and present state in agricultural soils where tobacco is cultivated, as heavy metal studies have mainly referred to polluted areas (Barandovski et al., 2008; Stafilov et al., 2010a, Stafilov et al., 2010b; Bačeva et al., 2011; Balabanova et al., 2011).

Trace elements deficiencies and toxicities in agricultural soil are associated with number of soil properties such as organic matter, type and amount of clay, pH and cation exchange capacity (CEC), all inherited from the soil parent material (Fadigas et al., 2010; Kabata-Pendias, 2011). These soil factors have influence of the quantity of trace elements available for mobilization and release or sorption in soil (Chen et al., 1999; Golia, 2001; Kabata-Pendias, 2011). Therefore, another objective of this study was to determine the most important soil factors (chemical and physical), which influence the content of total and aqua regia extractable elements of the soils used for tobacco cultivation in the Republic of Macedonia.

Aqua regia extraction giving for so-called pseudo-total content of the elements is widely used for determination of the contents of chemical elements associated with anthropogenic activities, while total digestion procedures are used for monitoring studies and estimations of possible long-term changes. Reliable values for trace element concentrations in aqua regia extraction are expected to be very different from the total concentrations. Here, aqua regia and total element contents of tobacco cultivation soil are presented and compared. The attempt was made to provide a basis for further monitoring of soil properties as essential for achieving sustainable land use, which will limit the negative impact of heavy metals.

Study area

Two years survey (2010-2011) was conducted in the well-known tobacco growing regions in Macedonia: Pelagonia region (PR), Southeastern region (SER) and Vardar Valley (VV) with 19 municipalities at 150 sampling sites (Figure 1a and b).

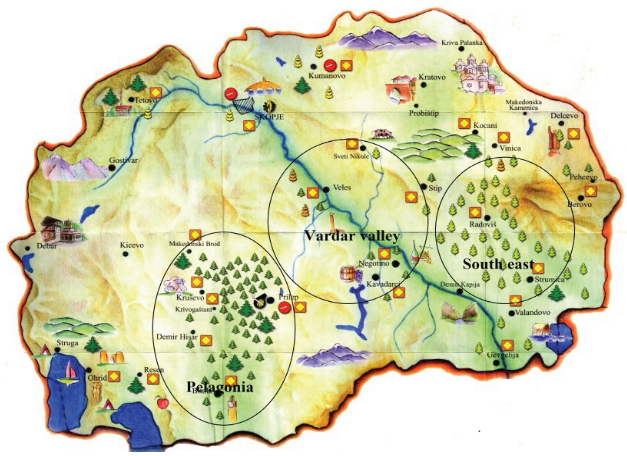

Fig. 1a. Tobacco growing regions in Macedonia (Pelagonia, South eastern region and Vardar Valley) provided by Scientific Tobacco Institute- Prilep

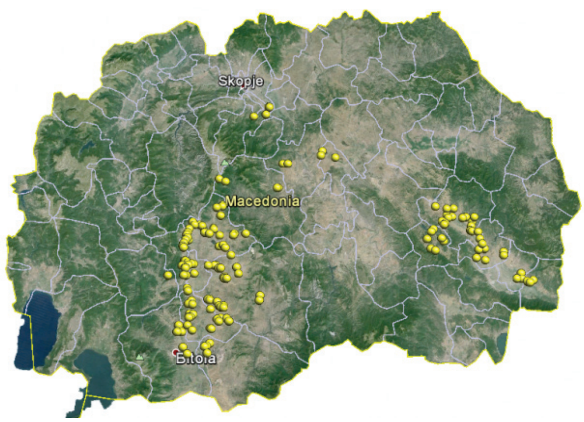

Fig. 1b. Sampling locations

The largest production is concentrated in Pelagonia region (Kabranova and Arsov, 2009) and is consisted of following municipalities: Prilep, Mogila, Kruševo, Krivogaštani, Bitola, Novaci, Demir Hisar, Dolneni. The region is characterized as a region with high population density in urban centers (238,000 inhabitants) and large agricultural area (total 4700 km^2). There are three mines in the region rich in lignite. All of the ash-forming elements (Si, Al, Mg, K, Ca, C, Fe, P, S, Ti, and Mn) are present in varying content in the Macedonian lignite and combustion waste products (mines and thermoelectrical power plant near the cities of Bitola and Kičevo) (Yossifova et al., 2009). The Pelagonian massif is a crystalline core with a continental type of Earth's crust built mostly of the oldest Precambrian formations (Barandovski et al., 2012). This geotectonic unit is separated from the neighboring units by regional and deep faults (north – Prilep field, south on lower elevation - Bitola field). The climate is mildly continental, with annual precipitation of 640 mm. Alluvial soils are covering this area of 302 km^2. River Black and its tributaries created this alluvial plain riddled with shallow riverbeds. Smolnitza (vertisol) soils are found with an area of 116 km^2 in the southern part of the valley. Delluvial, mainly loamy soils are present on the edges of the Pelagonia valley and on the slopes of hills, in the northern, northeastern edge of Prilep field. All terrains are with delluvial and alluvial soils.

Southeastern region (3492 km^2) tobacco production municipalities are Bosilevo, Vasilevo, Konče, Novo Selo, Radoviš, Strumica. This area represents a part of the Vardar structural zones during the Caledonian, subjected to strong tectonic processes during the Herzynian orogenesis and Alpine orogenesis (Rakicević et al., 1968; Hristov et al., 1965) with Precambian gneisses, Pliocene Lacustrine river terraces and alluvial sediments. Climate is continental Mediterranean, with annual precipitation of 583 mm. All terrain is characterized with alluvial and deluviall soil. Near municipality of Radoviš are Smolnitza (vertisol) soils that are very suitable for tobacco production. In this part of the country the appearance of some metals (Au, Mg, Al, Sc, Ti, V, Cu) in the air is related to the presence of a copper mine and flotation plant, "Bučim", near to the Radoviš town (Balabanova et al., 2010; Stafilov et al., 2010b; Balabanova et al., 2011). Influence from the former iron mine, "Damjan", has also been determined in this area (Serafimovski et al., 2010).

The Vardar zone is a large and important lineament structure of the Balkan Peninsula. Vardar Zone is the result of the destruction of the Grenville Earth's crust when it received its present day shape during the Alpine period (Barandovski et al., 2012). Annual precipitation is 635 mm. Vardar valley tobacco production region (17 km^2) is known for following municipalities: Studeničani, Veles, Čaška, Lozovo, Negotino, Kavadarci and Sveti Nikole. Due to the decreased tobacco cultivation in this area, samples were taken only from: Studeničani, Veles and Čaška. Veles region is known for its lead and zinc industrial activity in the nearest past. Several investigations of soil, vegetables and fruits produced in the region of Veles, concerned with contamination by lead, zinc and cadmium (Stafilov et al., 2010a; Stafilov et al., 2010b; Bačeva et al., 2011; Balabanova et al., 2011).

Materials and Methods

Soil composite samples from pedological profiles at fixed depth (0-30 cm) were taken from fields of each mentioned municipality. Samples were collected from 150 sites in each filed with two replicates. Samples were taken from cultivated soil after tobacco harvesting, and from uncultivated soils in the nearest vicinity. Longitude, latitude and altitude were noted for every sampling location. Samples pretreatment was done in accordance with ISO 11464:2006. First they were air-dried, and after that crushed and sieved through a 2-mm sieve.

Soil properties were determined, such as; mechanical composition (Đamić, 1996), pH (10390:2005), total nitrogen (11261:1995), organic matter with the wet oxidation method (Đamić, 1996), and calcium carbonate equivalent volumetrically (ISO 10693). Additionally total organic carbon (TOC) was determined by dry combustion (according to ISO standard 10694), electro conductivity was measured in a saturation extract, extractable phosphorus and potassium (ammonium lactate method) while the cation exchange capacity (CEC) was measured by the method described by Sumner and Miller (1996).

The following elements were analyzed: Al, Ba, Ag, As, Ca, Cd, Co, Mo, Cr, Cu, Fe, K, Li, Mg, Mn, Na, P, Ni, Pb, Sr, V and Zn. Obtained content of As, Cd, Co and Mo were under the detection limits and therefore they are not presented. Soil samples were digested by two methods: Aqua Regia extraction method (ISO 11466) and digestion for determination the total element content with HF method (ISO 14869-1). Aqua regia (HCl and HNO_3, 3+1) extraction method was done after digestion at 180ºC for 2 h. Soil samples (3.0000 g) were digested directly in the reflux digestion vessels where 21 ml HCl and 7 ml HNO_3 were added. The solution was brought to boil and the reflux was kept for 2 hours. The solution of each vessel was quantitatively transferred to 100 ml flasks.

For total digestion, soil samples (0.2500 g) were placed in a Teflon digestion vessel and were digested on a hot plate. In the first step, HNO_3 was added to remove all organic matter, then a mixture of HF and $HClO_4$ was added, followed by a third step where HCl and water were added to dissolve the residue. The solution was transferred quantitatively to the 25 ml volumetric flask. All reagents were of analytical grade (Merck, Germany). Analytical blanks were included in all extractions.

Instrumentation

The investigated elements were analyzed by the application of atomic emission spectrometry with inductively coupled plasma - AES-ICP (Varian, 715-ES). For the calibration a commercial standard mix solution (11355 - ICP Multi Element Standard IV, Merck) was used. Blank samples were used and processed simultaneously with soil samples. The limit of detection for the method was calculated as three times of standard deviation of the blank sample. The quality control of ICP-AES determination was performed by the standard addition method, and it was found that the recovery for the investigated elements ranged between 97.5 and 100.8%. The reference standard materials JSAC 0401 (soil) yielding values very close to certified values. Balabanova et al. (2010) give the optimal instrumental conditions.

Statistical analyses

The data were statistically analyzed using correlation analysis (Pearson correlation, two-tailed) and Factor analysis. Results from two replicates were averaged prior to statistical analyses. Correlation analysis was used to establish relationships between some soil characteristics and its heavy metal content. The degree of association of chemical elements in soil was also done with the linear coefficient of correlation. Statistical analyses were performed with the aid of IBM SPSS v 19.

Based on the results of normality tests and visual inspections of the distribution histograms, only total Al, Ag, K and Sr and pseudo-total K, Li and Mg follow a normal distribution of lognormal transformed data, respecting the general rule of trace element distribution in soils.

Results

Soil properties

Tobacco is grown on soils with different physical and chemical properties that have a direct influence on tobacco quality. Soil fertility is described as the content of certain nutrients such as OM, total nitrogen, available phosphorus and potassium, carbonates, pH and some biogenic microelements. Main average properties of soil samples from the investigated regions are given in Table 1. The results show that there are some statistical differences although not very significant in absolute values between treated soils and uncultivated control soils. Large differences were found in soils from Pelagonia region. Uncultivated soil showed moderate significant low content of OM, TN, clay and low values for pH and EC. In addition, significant high values of CEC were observed in soil from all three tobacco production areas compared with its appropriate control site. All examined soils have medium total nitrogen that varies from 0.01 to 0.40%. It was calculated that 80% of the soils were non-carbonate, 6% were poorly carbonate, 8% moderately and 6% strongly carbonate. TOC average content is 0.75% in SER, 0.9% in PR and 0.91% in VV.

According to texture, soils vary from silt loam to silt clay loams. Clayed soils were found only in the municipality of

Table 1
Mean values and standard deviation of soil properties of each production region

Site [a]	OM	TN	pH	Clay	Available P	Available K	CEC	EC
	%	%		%	mg/100 g		Cmolc/kg	µS/cm
PR	1.5±0.5	0.08±0.04	6.5±0.6	37.7±11.1	19.7±32.2	20.4±7.4	10.6±2.6	83 ±5 6
UPR	1.3±0.2	0.07±0.03	6.0±0.8	44.1±9.2	9.8±12.2	24.1±5.5	18.5±1.8	23±20
t	-5.5 **	-3.4 *	7.6 ***	-5.1**	ns	ns	-29.6***	10.38***
SER	1.3±0.3	0.06±0.02	6.7±0.5	36.4±11.9	12.5±23.5	21.8±4.6	9.68±2.3	78.92±55
USER	1.2±0.1	0.08±0.04	6.6±0.1	36.5±12.3	6.8±10.5	20.3±9.9	25.15±1.0	40.25±28
t	ns	ns	ns	ns	ns	2.15*	-43.07***	4.57 **
VV	1.6±0.3	0.07±0.02	7.7±0.8	45.9±7.2	24.5±25.3	31.7±14.3	11.8±1.9	215±109
UVV	1.0±0.3	0.05±0.04	7.8±0.1	51.9±6.5	17±11.2	26±9.9	21.4±1.0	269±56
t	5.7 ***	5.3***	ns	ns	ns	ns	-17.2***	ns

[a] PM: Pelagonia region, UPR: Uncultivated Pelagonia region; SER: South eastern region, USER: Uncultivated South eastern region; VV: Vardar valey, UVV: Uncultivated Vardar Valley. OM: organic matter; TN:total nitrogen; avail. P: available phosporus; avail. K: available potassium; CEC: cation exchange capacity; EC: electrical conductivity.
(Significant at P<0.05 - *, P<0.01 - **, <0.001 - ***, ns – not significant - P = 0.05)

Krivogaštani (Pelagonia region). Average values of soil pH were 6.5 and 6.7 for PR and SER, respectively. Average OM content is generally low to moderate, according to soil texture (Table 1). Available phosphorus and potassium concentrations varied differently (Figures 2 and 3). The highest values for available phosphorus (over 31 mg/100 g) were recorded in municipalities of Novaci and Demir Hisar (PR), and Caška (VV). Content of over 36 mg/100 g available potassium were recorded only in municipality of Veles (VV).

Elements content

Descriptive statistics for both total and aqua regia extractable contents of all analyzed chemical elements are given in Tables 2 and 3. Comparison of aqua regia contents to total

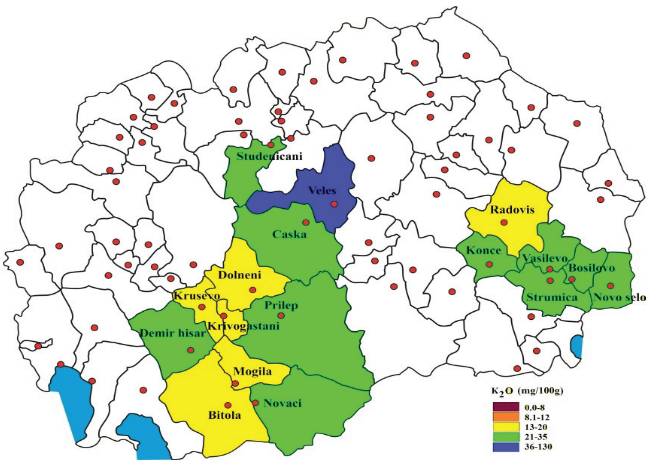

Fig. 2. Average content of available K, expressed as K_2O(mg/100g) in municipalities of R. Macedonia

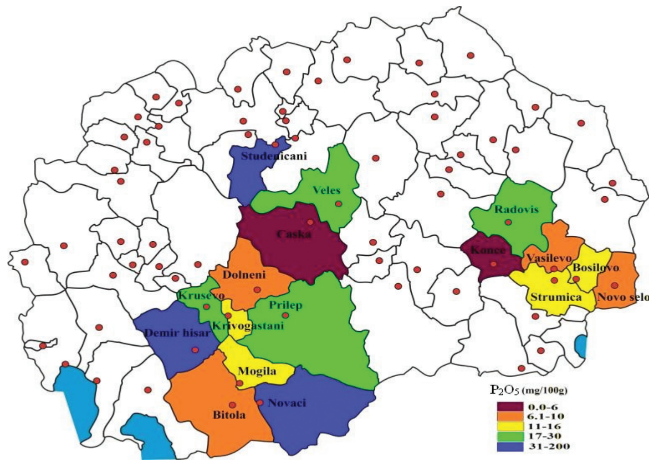

Fig. 3. Average content of available P, expressed as P_2O_5(mg/100g) in municipalities of R. Macedonia

Table 2
Descriptive statistics of chemical elements content after AR extraction (n=150). The values for Ca, Fe, K and Mg are given in %, for the rest of the elements in mg/kg)

	X_g	Md	s_a	A	E	Minimum	Maximum	P_{10}	P_{90}	CV
Ag	0.4	0.2	0.5	3.26	11.70	0.2	3.11	0.2	0.89	123
Al	1.6	1.4	0.6	1.33	1.96	0.6	3.6	0.9	2.4	38
Ba	94	85	35.6	1.13	1.38	32	231	56	147	38
Ca	0.4	0.3	0.5	6.30	49.11	0.1	5.2	0.2	0.6	131
Cr	29	22	26.5	4.06	19.93	8	194	11	45	90
Cu	16	14	9.7	3.43	20.21	5	88	8	25	60
Fe	1.8	1.8	0.7	0.51	-0.27	0.5	3.9	1.0	2.8	37
K	0.3	0.3	0.2	3.50	19.01	0.1	1.4	0.2	0.4	52
Li	10	9	5.1	1.84	4.71	3	34	4.1	16	54
Mg	0.3	0.3	0.1	0.75	1.57	0.1	0.9	0.2	0.5	40
Mn	477	441	166	1.55	3.95	184	1256	296	669	35
Na	40	36	18.5	2.04	6.30	10	133	22	61	46
Ni	22	17	18.3	3.37	13.94	5	127	9	36	84
P	434	366	260	2.56	8.97	144	1885	209	746	60
Pb	14	13	5.5	1.01	1.31	10	36	10	21	39
Sr	30	24	26.6	3.42	13.28	8	173	11	47	88
V	32	28	14.4	1.24	2.04	4	86	17	51	45
Zn	61	44	71.6	5.23	30.89	16	59	26	84	118

X_g – geometrical mean, Md - median, s_a – standard deviation, *A*-skewness, *E*-kurtosis, P_{10} 10 percentile, P_{90} 90 percentile contents is topic of many studies (Reimann et al., 2003 and Salminen et al., 2005). Aqua regia extraction, as referred for pseudo-total content of the elements is widely used for determination of the contents of chemical elements associated with anthropogenic activities. Total digestion procedures are often used for estimations of possible long-term changes. Overall, as it was expected, the results for the content of the analyzed elements after total digestion generally show more effectiveness in dissolving the soil compared with aqua regia extraction method (Tables 2 and 3). As it can be seen, total Ag, Al, Ba, Ca, K and Sr have three times higher values than the obtained content in soil after aqua regia extraction. Pseudo-total Na was very poorly extracted. Only contents of aqua regia extractable Fe, Mn, Pb, Zn and P do not much differ from total contents obtained by digestion with HF.

Aqua regia extraction represents the amount of elements that can be potentially labile in the environment better than those obtained after the HF digestion. That was clearly confirmed with the elevated levels of Cu, Pb, Zn and P in most of the analyzed samples extracted by aqua regia, manly connected with anthropogenic contamination. Although it is noticeable that Ni content determined after total digestion are higher that corresponding pseudo-content, significantly greater concentrations for aqua regia extraction were determined in VV production area (Tables 4 and 5).

The descriptive statistics for the elemental content in soil determined by both methods divided by three tobacco cultivation regions (PR, ESR and VV) are presented in Tables 4 and 5, respectively. Higher pseudo-total content of Ag, Ba, P, Sr in the samples from Pelagonia production region are correlated with diverse geological (background) and anthropogenic activities highly associated with uncontrolled phosphorus fertilization rates. In comparison with other two production regions, high coefficients of variation and elevated concentrations for aqua regia extractable: Pb (18 mg/kg), Ni (60 mg/kg), Mn (542 mg/kg) and Cr (62.6 mg/kg) were detected in VV. In the South-eastern region, highest concentrations of pseudo-total content of Al, Cu, Fe and Zn were detected.

According to production region distributions (Table 5), highest content of total Al, Ba, Ca, K, Mn, Na, P, Sr and V are generally found in PR. Average concentration of total Sr in this production region is two times higher than other two production regions. The strontium content could be influenced by chemical, mineralogical nature and physical environment of the soil in this region. Samples collected in Vardar Valley had the highest total content of Cr (64 mg/kg) and Ni (51 mg/kg). Total Zn average values ranged from 55-93 mg/kg in all collected samples, with the highest concentration of 1534 mg/kg measured in Konče (SER).

Table 3
Descriptive statistics of chemical elements content after HF digestion (n=150). The values for Ca, Fe, K, Mg and Na are given in %, for the rest of the elements in mg/kg

	X_g	Md	s_a	*A*	*E*	Minimum	Maximum	P_{10}	P_{90}	CV
Ag	0.5	0.5	0.2	0.82	0.42	0.2	1.3	0.2	0.8	50
Al	4.4	4.4	1.0	0.18	-0.15	2.3	6.8	3.1	5.5	22
Ba	318	296	116	1.47	3.23	133	764	194	442	36
Ca	9.9	9.3	6.2	1.41	3.55	1.5	41	3.3	18	63
Cr	49	44	32	3.92	24.56	13	292	19	75	65
Cu	18	15	9.6	1.46	2.08	5	53	9	30	54
Fe	2.3	2.2	0.8	0.88	0.61	0.9	4.9	1.5	3.5	34
K	1.0	0.9	0.3	0.79	0.31	0.4	2.0	0.6	1.4	35
Li	14	13	7.0	1.82	6.50	3.0	53.0	6.0	21.9	51
Mg	0.5	0.5	0.2	1.90	10.79	0.1	2.0	0.3	0.8	40
Mn	527	496	163	1.27	3.07	218	1268	357	719	31
Na	0.8	0.8	0.3	0.16	-0.18	0.1	1.7	0.4	1.2	41
Ni	25	20	18.9	2.87	10.23	5.0	124	10	42	76
P	453	377	295	2.62	9.33	73	2098	204	762	65
Pb	14	12	4.9	1.29	0.95	10	30	10	21	35
Sr	122	107	83.0	2.31	8.12	23	537	42	198	68
V	63	56	28.6	2.12	7.27	20	217	33	96	46
Zn	65	50	127	10.85	124.5	21	1534	31	79	193

X_g – geometrical mean, Md - median, s_a – standard deviation, *A*-skewness, *E*-kurtosis, P_{10} 10 percentile, P_{90} 90 percentile

Table 4
Descriptive statistic for chemical elements content in soil from three tobacco growing regions after AR extraction. The values for Ca, Fe, K and Mg are given in %, for the rest of the elements in mg/kg

	LOD	PR (n=96)			SER (n=42)			VV (n=12)		
	mg/kg	X_g	s_a	Min - Max	X_g	s_a	Min - Max	X_g	s_a	Min - Max
Ag	0.2	0.4	0.6	0.2 - 3.11	0.2	0.2	0.2 - 1.1	0.2	0.1	0.2 - 0.4
Al	0.9	1.5	0.5	0.6 - 3.2	1.8	0.7	0.8 - 3.6	1.5	0.4	1.0 - 2.1
Ba	10	100	36	42 - 231	83	33	32 - 174	79	23	55 - 129
Ca	10	0.3	0.2	0.1 - 1.6	0.4	0.8	0.1 - 5.2	0.9	0.9	0.2 - 2.7
Cr	1	25	20	8 - 194	29	18	8 - 80	64	46	15 - 166
Cu	0.5	16	8	5 - 39	18	13	6 - 88	13	4.1	6 - 22
Fe	1	1.7	0.7	0.7 - 3.4	2.1	0.6	0.8 - 3.9	1.6	0.5	0.5 - 2.2
K	2	0.3	0.1	0.1 - 1.4	0.4	0.2	0.1 - 1.0	0.2	0.1	0.2 - 0.3
Li	0.25	9	5	3- 30	11	6.5	4.2 - 34	10	3.2	4 - 16
Mg	0.5	0.3	0.1	0.1 - 0.9	0.4	0.1	0.1 - 0.6	0.4	0.1	0.2 - 0.6
Mn	0.5	480	177	184 - 1256	450	134	235 - 807	495	134	281 - 720
Na	1	41	19	10 - 133	41.9	18.8	18 - 90	25	6.4	15 - 38
Ni	0.5	18	12	6 - 111	19	9.4	5.4 - 45	60	35	14 - 127
P	1	457	280	172 - 1885	420	227	151 - 1186	302	141	144 - 612
Pb	10	13	5	10 - 28	15	5.7	10 - 30	18	7	10 - 36
Sr	10	37	31	10 - 173	18	8.8	8 - 59	21	10	9 - 44
V	1	30	14	5 - 86	36.9	15	12 - 80	26	11	4 - 40
Zn	1	55	46	23 - 461	64.4	46.9	16 - 267	54	21	21 - 105

LOD – limits of detection ,X_g - geometrical mean, s_a – standard deviation

Table 5
Descriptive statistics for total content of chemical elements (HF method) in soil from three tobacco growing regions. The values for Ca, Fe, K, Mg and Na are given in %, for the rest of the elements in mg/kg

	LOD	PR - Total (n=96)			SER –Total (n=42)			VV - Total (n=12)		
	mg/kg	X_g	s_a	Min - Max	X_g	s_a	Min - Max	X_g	s_a	Min - Max
Ag	0.2	0.5	0.2	0.2 – 1.1	0.5	0.3	0.2 - 1	0.4	0.2	0.2 – 0.7
Al	0.9	5	0.9	2.8 – 6.8	4.1	0.9	2 - 6	3.7	0.6	2.5 – 4.4
Ba	10	358	121	137 - 764	251	61	149 - 471	235	59	133 - 332
Ca	10	1.1	0.6	0.2 - 3	0.8	0.7	0.2 - 4	1	0.8	0.2 – 2.6
Cr	1	48	31	15 - 292	48	29	13 - 180	63	58	12 - 176
Cu	0.5	17	9	5 - 49	20	11	6 - 53	16	4.3	9 - 26
Fe	1	2	0.8	0.9 - 5	2.4	0.7	1 - 4	1.8	0.5	0.9 – 2.7
K	2	1	0.3	0.4 - 2	0.9	0.3	0.4 - 2	0.7	0.2	0.4 – 0.9
Li	0.25	14	7.6	3.4 - 53	13	6.5	12145	15	4.1	6 - 20
Mg	0.5	1	0.2	0 .4 - 2	0.6	0.2	0.2 – 1.1	0.5	0.1	0.2 – 0.7
Mn	0.5	551	171	218 - 1268	480	139	239 - 814	542	161	366 - 878
Na	1	1	0.3	0.1 - 2	0.7	0.2	0.2 – 1.1	0.5	0.2	0.3 – 0.9
Ni	0.5	22	13.6	7 - 124	25	20	5 - 117	51	29	7 - 96
P	1	475	320	140 - 2098	447	251	134 - 1309	299	151	73 -531
Pb	10	14	4.8	10 - 30	15	5.5	10 - 29	14	4.5	10 -22
Sr	10	151	89	26 - 537	72	29	26 - 147	64	29	23 - 109
V	1	66	32	27 - 217	61	20	24 - 112	43	14	20 - 67
Zn	1	59	84	16 - 593	93	228	23 - 1534	62	24	35 - 101

LOD – limits of detection, X_g - geometrical mean, s_a – standard deviation

To assess the dependence of the soil properties and the content of the analyzed elements the correlation analyses was performed on different variables (Table 6). Clay and CEC show moderate to strong correlations with elements from both digestion methods. OM has significant positive correlation with most of the aqua regia extractable elements, and positive significant correlation only with total Ba, Li and P. pH significantly correlates only with aqua regia extractable Ca, Ni and Mg and total Ni. No significant correlation was found among TOC and pseudo-total elements. Only total Ag, Ca, Sr, V and Zn significantly correlated with TOC.

In addition, in order to obtain a global view of the obtained results, a factor analysis was applied. Distribution patterns of total elements show five factors that describe 70.5 % of the total variance (Table 7). The first one is responsible for 28.48 % of the variance and was presented by V, Fe, Mn. Second factor is presented with Sr, Ba, Na, Al, Ca (17.31 % of the total variance), third with Cr, Ni and Mg. Fourth factor consist Li, Pb and K and finally fifth Zn and Cu.

Discussion

Soil properties

Hanson, (1999) and Bauder et al. (2007), reported the potential for reduction in infiltration rates resulting from various combinations of EC. Based on the results, only in VV region (Veles) few of the tested plots were slightly saline (EC > 360 μS/cm). This is probably due to quality of the water used for irrigation combined with the climate conditions. Generally, all analyzed soils were non saline, or low saline. The OM content was low as an intensive use of these soils. The literature data indicate that soils with lower OM content are a good environment for producing quality oriental aromatic tobacco (Filipovski, 1990; Pelivanoska, 2011). According to the results, 71 % of the samples showed low OM content, 24% were with average content and 2% with very low and good content. The total nitrogen content was low and similar to that of the OM. All soils had an adequate CEC for agricultural production use and none of them displayed a low capacity for nutrient storage (CEC < 10 cmol(+)/kg). These values are relatively low, and can be explained by low levels of organic matter and by low levels of clay. The soil pH was neutral in 58% of the soils, 16% were weakly acid and 20% of the samples were poor to moderately alkaline. The general conclusion is that the variability of the soil properties is due their geochemical origin represented by different types of land and long cultivation period.

Some of the soil properties (pH, CEC, TOC, texture) play important role in many pedogenic processes such as retention

Table 6
Correlation matrix of soil parameters v.s. extractable AQ and HF elements

	OM	Clay	pH	CEC	EC	TOC	OM	Clay	pH	CEC	EC	TOC
	AR extraction method						Total (HF extraction method)					
Ag	**0.309**	0.019	0.141	0.178	0.077	0.001	0.06	0.021	-0.089	0.019	-0.038	**0.469**
Al	**0.399**	**0.65**	0.146	**0.635**	**0.225**	0.002	0.154	-0.012	-0.059	0.074	-0.094	0.03
Ba	**0.495**	**0.621**	-0.011	**0.669**	*0.167*	0.003	**0.296**	0.093	-0.119	**0.221**	-0.022	0.001
Ca	*0.176*	**0.286**	**0.400**	**0.28**	**0.547**	0.02	-0.67	-0.055	0.124	-0.071	0.024	**0.208**
Cr	*0.161*	**0.303**	0.094	**0.282**	0.072	0.03	0.149	**0.27**	0.044	**0.254**	0.069	0.035
Cu	*0.195*	**0.509**	0.091	**0.434**	0.123	0.001	0.147	**0.414**	0.051	**0.347**	0.026	0.036
Fe	*0.162*	**0.508**	0.032	**0.415**	0.046	0.024	0.104	**0.427**	-0.014	**0.332**	-0.047	0.103
K	*0.188*	0.014	0.045	0.11	0.014	0.011	0.09	0.092	-0.074	0.107	-0.171	0.135
LI	**0.35**	**0.308**	0.13	**0.385**	*0.209*	0.002	**0.402**	**0.331**	*0.165*	**0.429**	**0.262**	0.001
Mg	0.157	**0.339**	**0.212**	**0.303**	0.155	0.028	0.117	**0.264**	0.048	**0.234**	-0.004	0.078
Mn	**0.212**	**0.493**	-0.008	**0.432**	0.017	0.005	0.18	**0.396**	-0.045	**0.352**	-0.05	0.014
Na	**0.26**	*0.196*	-0.062	**0.266**	**0.226**	0.001	-0.134	**-0.563**	-0.088	**-0.436**	**-0.315**	0.052
Ni	0.202	**0.399**	**0.293**	**0.366**	**0.318**	0.007	0.186	**0.344**	**0.228**	**0.322**	**0.274**	0.011
P	**0.214**	0.01	-0.005	0.123	0.015	0.004	**0.228**	0.065	0.012	0.167	-0.005	0.002
Pb	**0.243**	**0.488**	0.132	**0.447**	**0.221**	0.001	0.198	**0.233**	0.022	**0.25**	0.094	0.008
Sr	*0.205*	0.069	-0.058	0.16	0.061	0.006	0.04	-0.162	-0.1	-0.081	-0.117	**0.312**
V	0.061	**0.349**	-0.029	**0.259**	-0.086	*0.230*	0.018	**0.355**	-0.032	**0.240**	-0.12	**0.414**
Zn	*0.163*	**0.214**	0.049	**0.226**	0.046	0.023	0.022	0.103	0.007	0.078	-0.025	**0.396**

Italic numbers - Correlation is significant at the 0.05 level (2-tailed); Bold numbers - Correlation is significant at the 0.01 level (2-tailed) and absorption of metal elements via OM and fine particulate matter (Alloway, 1999; Kabata Pendias; 2011; Saint-Laurent et al., 2013). The Pearson correlation coefficients relating to associations between soil properties and element content of all analyzed soil samples are given in Table 6. Statistically, the correlation analyses among different variables (OM, clay, pH, CEC, TOC and EC) show poor, moderate to strong correlations with elements from both extraction methods. The correlation coefficients considered significant were only those with probability level smaller than 1 and 5 % ($P<0.01$ and $P<0.05$).

Clay and CEC revealed strong correlations ($P<0.01$) with content of most total and aqua regia extracted elements (Table 6). The positive correlation of trace metals (Co, Cu, Ni, Pb, and Zn) with clay content of soils is, according to Kabata-Pendias (2011), responsible for increasing their levels in the B soil horizons where clay is translocated from the A soil horizon. Ma et al. (1997) found the best correlation between total trace element content and clay content and little correlation between total trace element content and organic carbon, CEC and pH.

Several studies have been conducted to study the influence of soil properties on the total trace element contents of soils (Ma et al., 1997; Burt et al., 2003; Chen et al., 1999; Tack et al., 1997; Kabata-Pendias, 2011). Burt et al. (2003), found the best correlations between the total trace element concentrations and total Fe, total Al and CEC. According to Tack et al. (1997), clay content and organic carbon had significant correlations with the total trace element content of the topsoil. In our study, pH significantly correlates only with aqua regia extractable Ca, Ni and Mg and total Ni. No significant correlation was found among TOC and pseudo-total elements content. Only total Ag, Ca, Sr, V and Zn significantly correlated with TOC (Table 6).

Some authors (Alloway, 1999; Kabata Pendias, 2011) stated that the main factor of heavy metal migration is dissolved organic matter DOM. Here, OM indicated positive correlations with the most of the elements extracted by aqua regia, except for V and Mg. That was not case with total element content, where strong correlations between OM was detected only for Ba, Li, Ni and total P.

While correlations between pH, EC, TOC and most of the total and aqua regia extracted elements were generally not significant ($P<0.05$), there was a strong positive correlation among soil parameters: organic matter content with CEC (r = 0.809) and CEC with clay content (r = 0.874). The relationships between the elements appear complex and difficult to explain, however strong correlations were present among

Table 7
Rotate component matrix (n=150), 18 selected elements

Element	Component					
	F1	F2	F3	F4	F5	Com
V	**0.926**	0.051	0.193	-0.054	0.084	90.8
Fe	**0.899**	-0.016	0.32	0.048	0.065	91.8
Mn	**0.771**	0.128	0.177	0.207	0.042	68.7
Sr	0.004	**0.923**	-0.017	-0.134	-0.009	87.1
Ba	-0.055	**0.789**	0.234	0.293	0.024	76.7
Na	-0.228	**0.651**	-0.516	-0.066	-0.033	74.8
Al	0.326	**0.619**	-0.169	0.143	-0.142	55.9
Ca	0.444	**0.608**	0.042	-0.229	0.007	62.1
Cr	0.306	0.005	**0.886**	0.036	0.004	87.9
Ni	0.125	-0.128	**0.878**	0.007	0.201	84.5
Mg	0.487	0.271	**0.656**	0.152	0.089	77.1
Li	-0.037	-0.148	0.186	**0.78**	-0.087	67.5
Pb	-0.015	-0.094	0.015	**0.746**	0.036	56.6
K	0.149	0.245	-0.064	**0.581**	0.069	42.8
P	0.26	0.323	0.309	**0.400**	0.175	45.8
Ag	0.186	0.091	-0.156	0.241	0.214	17.1
Zn	-0.052	-0.051	0.111	-0.034	**0.951**	92.4
Cu	0.508	-0.115	0.32	0.177	**0.706**	90.3
Var	28.48	17.31	10.33	7.41	7.02	70.5

Com - Comunality (%), Var - Variance (%)

pseudo-total Al, Ba, Cr, Cu, Fe, Mn, K and all other analyzed elements. In contrast, aqua regia Ca showed no significant correlation with all investigated elements. All our results are comparable with previously published data by Chen et al., 1999; Hamon et al., 2004; Soriano-Disla et al., 2013 where trace element content correlated poorly with pH, TOC, even CEC, and had high inter-element correlation.

Elements

The study on agricultural soils of Europe (Salminen et al., 2005; Soriano-Disla et al., 2013) show that median values of obtained metals and metalloids are comparable to those obtained from the present study. Median content of all determined metals are not exceeding the contamination limit except for Ni measured in Vardar production region and total Ba content from all production regions (The new Dutch list, (http://www.contaminatedland.co.uk/std-guid/dutch-l.htm#KEYWORD-ONE)). All studied elements have a wide variation in their content, and Ag, Ca, Cr, Zn, Cu, Ni and Sr (Tables 2 and 3) show the greatest.

As it can be seen in Tables 2 and 4, pseudo-total concentrations of few elements sampled from different tobacco regions show anomalies, although their median concentrations do not exceed the contamination level. Such anomalies were observed in Cr, Cu, Ni and Zn content from Pelagonia production region. Few samples from Dolneni, Krivogaštani and Kruševo had high Cu content. In the same sampling locations from Dolneni, very high Cr, Ni and Zn content were obtained. This can be correlated with geological background as most of the lithogenic elements had high concentrations. Nevertheless, anthropogenic activities cannot be excluded because of the high P content measured in this location. In southeastern tobacco production region, high concentrations of Cu, Ni and Zn were observed in the sampling points from the municipality of Radoviš. Cu concentration can be correlated with the presence of a copper flotation plant, "Bučim", near the town Radoviš and mine. Content above the contamination level for Ni were detected in most of the samples from the Vardar Valley production region. High Cr content occurred in the samples with the highest Ni concentration in two sampling spots located in municipality of Čaška. Nickel status in soils is highly dependent on its content of parent rocks, which for this region is explained by Stafilov et al. (2010a). However, the content of Ni in surface soils also reflects soil forming processes and pollution (Kabata-Pendias, 2011).

For total element distribution, five factors have been identified and matrix of rotated factor loadings is given in Table 7. The first component (Factor 1) presented by V, Fe, Mn is strongest factor representing chemical elements that are probably naturally distributed. In general, Fe and Mn are not contaminant elements and are important and essential crop micronutrients. The Fe content of soils is both inherited from parent rocks and the result of soil processes and it concentration in soils is from 0.5 to 5%. Fe in European topsoil average is 2.2 % (Salminen et al., 2005), and in cultivated soils in Macedonia (VV cultivating area) 2.4 % (Stafilov et al., 2010a). The highest content of this group of elements were measured in samples from PR (Table 5). Content of 5 % Fe was measured at Bitola and Mogila. This is explainable with "Suvodol" open coal deposit as a part of Pelagonian massif. High Mn levels are often reported for soils rich in Fe or organic matter and for soils from arid or semiarid regions (Kabata-Pendias, 2011). On the European scale, the range of Mn average content of topsoil soil units is 524 mg/kg (Salminen et al., 2005) and 496 mg/kg from our study (Table 3). The average V contents of soils worldwide have been calculated to vary from 18 ppm for histosols to 115 ppm for rendzinas (Kabata-Pendias, 2011). In Macedonia (Stafilov et al., 2010a) average V content is 71 mg/kg and 63 mg/kg reported from our study.

Factor 2 (Sr, Ba, Na, Al, Ca) also represents chemical elements that are probably naturally distributed. Median values from agricultural soils are following: 190 mg/kg for Sr, 460 mg/kg for Ba, 22 % Na, 6.1 % Al and 3.1 % for Ca (Stafilov et al., 2010a). Sr content of soils is highly controlled by parent rocks and climate (Kabata-Pendias, 2011). Higher content of Sr (537mg/kg) and Ba (700 mg/kg) were determined from samples collected from PR (municipalities of Dolneni and Kruševo). Association of Ba in this group indicates small anthropogenic influence, although Ba is part of acid magmatic rocks and commonly ranges in content from 400 to 1200 mg/kg (Kabata-Pendias, 2011). This author presents that the Ba budget in rural soils shows a steady increase from aerial sources and P fertilizers increases its output. The spatial distributions of Ca, Na and Al content levels result are strictly connected to the nature of the pedogenic materials and to the evolution processes of the different types of soil.

Factor 3 represented by Cr, Ni and Mg describes elements primarily affected by lithological background, but anthropogenic influence as well. The presence of high clay content and human activities can increase the normal content of Cr in soil (Micó et al., 2006). The Cr mean values are not high enough to indicate contamination, although slight increase in Cr content occurred in PR (Dolneni), VV (Čaška) and Radoviš (SER).

Fourth factor is consisted of Li, Pb and K. Regardless to Li, Pb and K in the ecosystem are introduced through anthropogenic activities. K comes into soil mainly with uncontrolled rates of K fertilizers. Fifth factor is the weakest chemical association of Zn and Cu that are consequences of human activity. Anomalies were measured in the municipalities of Konče and Kruševo.

Conclusions

In the recent few decades, tobacco production in Macedonia has intense agriculture increasing the use of fertilizers and pesticides. Consequently, the contaminant content such as trace elements is increasing. Therefore, it becomes crucial to better control all sources of pollution of agricultural soils. The objective of our study was to clarify the quality of the soils used for cultivation of sun cured oriental tobacco and monitor basic soil properties as essential for achieving sustainable land use.

All sample locations included more regions of the country, so there is a great diversity in soil parameters. The soil content of all detected elements pointed out levels, which are typical of agricultural and low anthropogenic pressure areas. Only some chrome, nickel and barium levels in the surroundings of municipalities Dolneni, Radoviš and Caška exceed the contamination limit. The obtained results showed that there were significant correlations between OM, CEC and clay with aqua regia extraction method. Results from HF diggestion method compared to aqua regia method show more effectiveness in dissolving the soil with three times higher content for total Ag, Al, Ba, Ca, K and Sr. Aqua regia extraction procedure was more effective for following elements: Cu, Mn, Ni, Pb and P. Generally, all analyzed samples are a good base for the production of high-quality small-leaf oriental tobacco. Moreover, some adjustments are needed that can largely be achieved through appropriate fertilization rate recommendations. Given that soil fertility is a dynamic area clearer picture of the current state of all tobacco cultivated soils can be given after further and extended monitoring during the next years.

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