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ORIGINAL PAPER

EVALUATION OF THE CHEMICAL COMPOSITION OF SOIL AS WELL AS VINE LEAVES AND BERRIES FROM SELECTED COMMERCIAL FARMS IN THE REPUBLIC OF TAJIKISTAN*

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Abstract

The Republic of Tajikistan is a country with a considerable fruit production potential. One of the factors most frequently implicated as limiting agricultural development, not only in the Republic of Tajikistan but also in other Central Asian countries, is the insufficient development of quality management systems in primary production, which causes difficulties in product exports. Development of a model based on soil properties which would enable evaluation of possibilities of grape production is an important element of supporting a decision-making process in the conditions of quality management systems in primary production. The aim of the study was to evaluate chemical composition of grapes and vine leaves, and the the content of assimilable forms of elements in soil. In 2018, soil samples as well as vine leaf and berry samples were

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collected in the Republic of Tajikistan, in the area of Dushanbe and Khujand. In the selected plant and soil samples, the content of Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr and Zn was determined. The elements were determined by inductively coupled plasma atomic emission spectroscopy. The results reveal a relatively low potassium, phosphorus and magnesium content in plants and a high content of Cu, Fe, Ni, Pb, Cr, and Al in the grapes under analysis. In no case did the content of potentially toxic elements exceed critical values for products intended for consumption (FAO/WHO 2011). Determination of assimilable forms of elements in soil extracted by means of acetic acid is a useful method of evaluating their abundance in soil under analysis. For most of the elements being tested, statistically significant correlation factors were reported between the content of elements in vine leaves and berries. As regards Sr, Cu, Na, Cd, Zn, As, Al, B, Ba and Pb, a statistically significant relationship was found between their content in leaves and berries.

Keywords: bioconcentration, microelements, macroelements, Tajikistan, grape quality.

INTRODUCTION

One of more important quality criteria concerning food and agricultural products is the content of elements, both macroelements and microelements. In addition, the amount of potentially toxic elements is crucial for food safety (Niemiec et al. 2017, Milićević et al. 2018). In accordance with modern quality management standards in primary production, the undertaking of cultivation in new areas should be preceded by a risk analysis related to threats to quality and product safety (Wang et al. 2018, Niemiec et al. 2019). Input data for such risk assessment consists of information about field history, chemical composition and physico-chemical properties of soil. According to the soil chemical composition, one can plan cropping patterns as well as a fertilisation strategy, compliant with the principles of rational management of plant nutrients (Niemiec et al. 2015). From the point of view of production management, it is crucial to select a suitable plant, based not only on its economic potential, but also on the risk of contamination with substances concentrated in soil (Szeląg-Sikora et al. 2019). Complex risk evaluation related to the inclusion of excessive amounts of heavy metals in the human food chain is a key element of effective environmental management. Due to the occurrence of numerous risk factors involved in possible excessive accumulation of elements in plant tissues, it is very difficult to apply risk models developed in particular climatic, soil and technological conditions, considering various production circumastances (Wang et al. 2018, Kocira et al. 2019). Therefore, risk evaluation with regard to trace elements should be conducted for specific soil and climate settings. The accumulation of elements in live organisms' tissues depends not only on their total quantity in a biotope, but also on soil properties, plant species and the course of weather conditions. Plant cultivation on soils with an elevated level of trace elements, unregulated pH and in areas contaminated with organic compounds may result in obtaining products hazardous to consumer health. Regardless of the number of contamination sources and intensity of their impact on shaping chemical properties of soils, in the context of quality management, the most important task is to translate the chemical composition of soil into the chemical composition of an agricultural product used for existing or future food purposes (Kumar et al. 2019). In developing countries, where the scope of official control of agricultural production is limited, there is a high risk that production will take place in sites with an elevated level of xenobiotics in soil or in water used for irrigation. Production of fruit and vegetables in developing countries often involves using sewage for irrigation and fertilisation (Oguri et al. 2018). Agricultural cultivation is stimulated by opportunities to sell products and by tradition. Products introduced into local markets are usually not subject to official control or inspection of retail chains. Internationalisation of commercial farms in developing countries gives rise to a need to implement a quality management and production safety system. This is the first step twoards the development of formal quality management systems.

The Republic of Tajikistan is a state with a considerable fruit production potential. Good climatic conditions in this country enable production of high quality apricots, grapes, mulberries and other fruits with high sugar content. One of main limitations of the agricultural growth in this scope is the insufficient development of quality management systems, which makes it very difficult to export products. A fundamental issue relating to the implementation of a quality management system is the organisation of production in areas which are not contaminated and where products of a desired quality can be obtained. Proper grapevine nutrition with microelements is highly important for shaping fruit quality. Acuña-Avila et al. (2016) stated that higher strontium, manganese and lead contents are positively correlated with the content of antioxidants in fruits. On the other hand, Ferrari et al. (2019) pay attention to a high risk of elevated copper and chromium content in vine leaves and berries.

Currently, there are few studies concerning the quality of grapes produced in the Republic of Tajikistan in relation to soil quality. Development of a model which would enable an assessment of possible grape production on the basis of soil properties is an important element of supporting a decision-making process with regard to quality management systems in primary production. The assessment of dependencies of chemical composition in vine leaves and berries under Tajikistan's climatic and soil conditions will make a crucial contribution to supporting production technologies with respect to fertilisation. Chemical composition of grapes is an important indicator of their quality in the context of using them as raw material for wine production and in the context of storage properties.

Grapevine is a plant characterised by a high bioconcentration potential of elements contained in soil (Milićević et al. 2018, Ferrari et al. 2019). Pepi et al. (2017) proposed a method of identifying the origin of grapes on the basis of their chemical composition. The cited authors reported a statistically significant dependence between the strontium content in soil and fruits.

In addition, they drew attention to a possibility of using Ba, Ca, Mg, Al, K, Zn, B and Ni contents in soil and berries to identify fruit origin.

The goal of the study was to evaluate the chemical composition of berries and leaves, as well as contents of assimilable forms of elements in soil. Another goal was to assess the bioconcentration factor of the selected elements in leaves and berries.

MATERIAL AND METHODS

In order to achieve the research goals, soil, berry and leaf samples were collected in the Republic of Tajikistan, in the area of Dushanbe and Khujand. The samples were collected from 16 farms producing grapes for the internal market. The dessert vine variety Pobeda was used for the research. The farms under analysis did not have an implemented quality management system nor had they made any soil tests to design the fertilisation regime. Laboratory samples were collected from a uniform production surface ranging from 0.1 to 1 ha, depending on a particular farm. Soil samples were collected from the depth of 0 to 25 cm. From each farm, 4 laboratory samples were collected. One composite soil sample consisted of 15 primary samples, whereas one compsite sample of berries originated from 15 grapes. Laboratory samples were formed by reducing the weight of composite samples. Laboratory samples of berries and leaves were dried at a temp. of 65°C, homogenised and subjected to wet mineralisation in a closed system by means of microwave energy. A microwave system made by Anton Paar Multivawe 3000 was used for mineralisation. Berry and leaf samples were mineralised in a mixture of nitric acid solution (V) and dihydrogen dioxide at a volume ratio of 1:3. The weight of an analytical test portion was max. 0.5 g of dry weight. The soil samples were dried and sieved through a sieve with a mesh of 1 mm. The tested elements were extracted from soil by means of acetic acid at a concentration of 0.03 M dm^{-3} (Quevauviller 2002). In this study, acetic acid was selected as the extractant in an effort to develop a universal method for assessment of soil richness in microelements, macroelements and heavy metals in the study area. The use of a universal method is dictated by economic factors. Concentration of the elements under analysis in the solutions was determined by means of the atomic emission spectroscopy method, using an Optima 7600 instrument made by Perkin Elmer. The lengths of waves, by means of which the concentration of the tested elements and limits of determination with regard to the methods used were determined, are presented in Table 1. To control the accuracy of elemental analyses, certified reference materials IAEA-V-10 were used. Table 1 shows the results of reference material analyses and the recovery value, on the basis of the analyses performed in 4 replications. Based on the acquired results, bioconcentration factors of particular elements were calculated. Each biocon-

Table 1

Parameters of the analytical method

Parameters	Wavelengths	Limit detection	Content in certificated material	Measured	Recovery
	(nm)	(mg dm^{-3})	(mg kg^{-1})	(mg kg^{-1})	(%)
Al	396.153	0.0315	685	663.5	97
As*	188.979	0.0134	-	-	-
B*	249.772	0.0061	-	-	-
Ba	233.527	0.0042	6	108.7	109
Ca	317.933	0.01	21600	22896	106
Cd	228.802	0.0027	0.03	0.0315	105
Cr	267.707	0.0071	6.5	6.76	104
Cu	327.393	0.0097	9.4	10.058	107
Fe	238.204	0.0046	185	179.45	97
K	766.490	-	21000	19740	94
Li	670.784	0.0826	1.15	1.189	103
Mg	285.208	0.0016	1360	1414.4	104
Mn	257.608	0.0014	47	46.53	99
Na	589.592	0.069	500	485	97
Ni	231.604	0.0151	4	3.84	96
P	213.617	0.076	2300	2231	97
Pb	220.353	0.0425	1.6	1.696	106
Sr	407.771	0.00048	40	96,4	96
Zn	206.200	0.0059	24	23.52	98

The element is not included in the reference material.

centration factor (BF) was calculated by dividing the concentration of a given element in dry mass of leaves or berries by the content of assimilable forms of this element in soil.

$$\text{bioaccumulation coefficient} = \frac{\text{metal concentration in leaves or berries (mg kg}^{-1}\text{)}}{\text{metal concentration in soil (mg kg}^{-1}\text{)}}$$

In addition, Spearman's rank correlation values at significance levels of 0.05 and 0.1 were calculated between concentrations of the selements in soil, leaves and berries.

RESULT AND DISCUSSION

The results of the study indicate considerable changes in the content of the elements in particular samples, both in soil and in the studied parts of plants (Table 2). An average aluminium content in grapes was

Table 2

The content of elements in the soil, grape leaves and berries and the values of bioaccumulation coefficients

Element	Content in soil	Content in leaves	Content in berries	Bioconcentration factor in leaves	Bioconcentration factor in berries
	(mg kg^{-1})				
Al	2.270	470.1	15.51	206.3	6.829
Range	2.090-2.720	371.5-551.5	12.51-18.48	150.4-263.9	5.359-10.32
As	0.080	0.173	0.0452	2.149	0.570
Range	0.060-0.100	0.067-0.242	0.021-0.058	1.111-3.333	0.417-0.833
B	1.009	20.09	13.90	16.52	13.00
Range	0.400-1.560	7.283-49.60	9.250-19.18	7.027-32.63	9.571-18.13
Ba	3.745	16.46	1.530	4.679	0.517
Range	1.430-6.050	5.908-32.98	0.792-3.410	3.476-7.759	0.202-1.166
Ca	4067	17203	793.8	4.303	0.198
Range	3617-4446	15466-19758	607.8-1005	3.726-4.863	0.160-0.262
Cd	0.065	0.033	0.017	0.504	0.244
Range	0.038-0.092	0.025-0.042	0.008-0.033	0.362-0.801	0.100-0.385
Cr	0.009	0.981	0.374	114.9	44.94
Range	0.006-0.013	0.667-1.150	0.333-0.400	88.46-160.7	30.77-63.89
Cu	0.394	8.860	3.498	25.98	10.26
Range	0.170-0.720	1.725-26.13	2.117-4.592	2.581-70.43	4.731-15.35
Fe	0.160	406.3	55.38	3040	359.3
Range	0.090-0.260	240.2-531.9	32.18-135.2	1345-5397	247.5-711.4
K	647.2	4170	7368	7.583	14.44
Range	293.7-1317	2779-6223	6397-8574	2.889-10.18	5.989-25.57
Li	0.086	2.265	0.164	25.91	1.950
Range	0.070-0.100	0.925-5.575	0.142-0.192	10.42-61.94	1.500-2.619
Mg	244.0	2055	341.8	8.401	1.372
Range	195.9-288.5	1363-3008	273.5-446.4	4.979-14.38	0.999-1.599
Mn	3.866	86.73	4.445	26.98	1.294
Range	1.990-7.580	62.98-132.6	2.992-5.867	9.591-59.38	0.562-1.895
Na	66.93	308.0	65.26	4.009	1.192
Range	43.32-135.2	129.6-658.3	28.11-106.3	2.411-6.101	0.261-2.241
Ni	0.035	0.717	0.136	20.71	3.796
Range	0.030-0.050	0.475-0.867	0.083-0.250	14.83-26.11	2.708-6.250
P	542.0	577.3	883.5	1.653	2.671
Range	115.0-957.2	466.6-703.4	722.7-1133	0.600-4.057	0.767-6.284
Pb	0.024	1.099	0.234	90.37	17.89
Range	0.007-0.049	0.375-2.317	0.133-0.441	13.39-289.6	4.150-55.10
Sr	21.21	203.6	6.783	8.774	0.322
Range	16.10-30.31	97.28-456.3	3.925-12.89	5.561-15.19	0.218-0.446
Zn	0.150	21.25	7.804	145.5	46.79
Range	0.090-0.230	9.367-51.11	2.617-28.54	46.83-278.1	15.04-124.1

2.351 mg kg^{-1}, whereas in leaves it was 470 mg kg^{-1} (Table 2). Milićević et al. (2018) determined the content of this element in grapes from Serbia to be about 10 times lower, while finding a similar dependence between the concentrations of this element in fruits and leaves. Acuña-Avila et al. (2016) reported about 56 mg kg^{-1} of this element in different grape varieties from Mexico. Lachman et al. (2013) found a considerable impact of a variety on the content of macroelements and microelements in grapes. The authors reported the content of potassium comparable to that found in our study. The current research results indicate a low calcium, magnesium and phosphorus content in the studied grapes. Lachman et al. (2013) found several times higher amounts of these elements in grapes from different regions of the Czech Republic. Milićević et al. (2018) determined about twice as much calcium and magnesium in vine leaves, whereas concentrations of these elements in berries were several times higher than obtained in our study. Also, Panceri et al. (2013) reported a higher macroelement content in grapes grown in Brasil than observed by us in Tajikistan. Also, Acuña-Avila et al. (2016) demonstrated average amounts of calcium, magnesium, potassium and sodium to be slightly higher than observed in this study, namely they detected 869 Ca, 399 Mg , 12 060 K and 244 Na in mg kg^{-1} of dry fruit mass. Average potassium, calcium and magnesium concentrations were comparable to those determined in grapes from Argentine. Insufficiently high content of macroelements has a negative effect on the quality of grapes. Apart from problems such as decreased supplies of quality grapes and grape products to consumers, an excessively low content of macroelements has a negative impact on fruit storage capabilities. The macroelement content found in our study is generally lower than specified in scientific literature, although our results do not indicate any risk of plant malnutrition and a lower quality of products intended for food purposes.

Concentrations of iron, aluminium, copper, lithium, nickel, lead and cadmium determined in this study, both in leaves and fruits, were much higher than those found in grapes from Serbia, according to Milićević et al. (2018). The average lead, cadmium, chromium and nickel content in dry mass of the grape samples we analysed was 0.234 mg kg^{-1}, 0.017 mg kg^{-1}, 0.374 mg kg^{-1} and 0.136 mg kg^{-1}, respectively. The reported concentrations of lead, nickel and chromium were higher than presented by other authors. Nie et al. (2016) reported the content of these elements in grapes from China to be several times lower than determined in the currennt study. Fang and Zhu (2014) determined the content of lead, cadmium and copper comparable to the levels achieved in our analyses, whereas the chromium content was about 3 times higher in grapes from the Zhejiang Province in China. The authors reported the chromium, copper, cadmium and lead content in vine shoot at 2.57, 6.69, 0.21 and 1.95 mg kg^{-1}, respectively. The content of chromium in leaves of the grapes we studied was ca. 3 times higher than in berries, while the concentrations of copper and cadmium were about 2 times higher, and the lead content was 5 times higher than in berries.

Fang & Zhu (2014) found similar quantitative relations between the above elements in shoots and berries of plants grown in soil in these elements. The content of Al, Ba, Cu, Mn, Zn, B and Fe determined in our research was higher than reported by Acuña-Avila et al. (2016) and Chopin et al. (2008). Fabani et al. (2017) identified a several-fold higher Li and B content in berries of several grapes species from Argentina. However, the content of iron and zon was 5-fold lower, and Mn, Cu and Sr concentrations were comparable to the ones determined in our experiment.

Grapes are rich in microelements and macroelements, and they constitute a potential source of those elements for people. However, their bioavailability is limited, which is pointed out by de Silva Haas et al. (2019). Nonetheless, the mineral content in grapes is an important quality parameter of fruits.

Quantities of assimilable forms of elements in soil depend on the extracting agent being applied (Milićević et al. 2018). These authors suggested that it is impossible to indicate an optimum extracting agent to determine assimilable forms of all elements in vine cultivation. They reported the concentrations of aluminium, iron, barium and manganese extracted from soil by means of acetic acid being almost ten times higher than values reported in our study. On the other hand, higher amounts of boron, copper and strontium were found in soil in our experiment than given by the quoted authors. As for the remaining elements, their soil content was comparable. The bioconcentration factor is a useful indicator in evaluating the risk of incorporating excessive amounts of trace elements into the human food chain (Niemiec et al. 2018). The bioconcentration factor determines the potential of absorbing the elements contained in soil by plants. The bioconcentration factor depends on plant species, soil properties and weather conditions during the plant growing period. The bioconcentration factor of the elements studied in grapes ranged from 0.198 to 359.3. The highest value of this parameter was reported for iron. In the case of B, Pb and K, the value of this parameter ranged from 10 to 20. For most of the analysed elements, the value of the bioconcentration factor in relation to their content in fruits was below 1 (Table 3). The study results show that the bioconcentration factor of the elements determined in leaves ranged from 0.504 to 3040. The highest value of that parameter was reported for iron, whereas the lowest one was achieved for cadmium. Milićević et al. (2018) stated much higher values of the bioconcentration factor in leaves of grapes coming from Serbia with respect to Ba, Ca, Cu, Mg and P, whereas in the case of Cr, Cu, Fe, Mn, Ni and Zn, the values of this parameter were several times lower than reported in this study, for grapes from the Republic of Tajikistan. The research results show statistically significant positive correlations between boron, barium, chromium, sodium, strontium, zinc, phosphorus and arsenic in soil and in leaves of the studied plants (Table 3). Slightly lower values of the correlation coefficient were found between the content of assimilable forms of elements in soil and grapes. In addition, a statistically significant

Table 3

Values of the correlation coefficient between elemental content in soil (S), in vine leaves (L) and berries (B)

Values	Al	As	B	Ba	Ca	Cd	Cr
L/B	0.548*	0.778**	0.596**	0.637**	0.235	-0.530*	0.348
L/S	-0.841**	0.562*	0.661**	0.781**	0.080	0.147	0.624**
B/S	-0.263	0.514*	0.593**	0.109	0.119	0.359	0.247
	Cu	Fe	K	Li	Mg	Mn	Na
L/B	0.734**	0.429	0.274	0.172	0.288	0.276	-0.565*
L/S	-0.190	-0.204	0.314	0.283	-0.522*	-0.330	0.758**
B/S	0.177	0.593**	0.122	0.180	0.300	0.000	-0.548*
	Ni	P	Pb	Sr	Zn		
L/B	0.351	-0.361	0.582*	0.872**	0.811**		
L/S	0.163	0.540*	-0.360	0.793**	0.411		
B/S	0.503*	0.120	-0.335	0.642**	0.506*		

** Statistically significant correlation coefficient at p=0.01, * statistically significant correlation coefficient at p=0.05

negative correlation was reported between the aluminium content in soil and leaves of the plants. A statistically significant correlation was found between the content of boron, iron, nickel, strontium zinc and arsenic in soil and berries (Table 3). In the case of iron, the value of the correlation between its content in soil and fruit was reported at the level of 0.593, compared to – 0.204 for its content in soil and in leaves. Dependences between the content of elements in soil extracted by means of acetic acid and their content in plants are very strong and indicate usefulness of this extraction method when evaluating soil abundance in macro-and microelements. Pepi et al. (2017) state that vine plants are characterised by a high potential of element binding, in proportion to their contents in soil. Similar conclusions were drawn by Ferrari et al. (2019), who analysed grape waste in the context of its use for fertilisation purposes. The chemical composition of plant leaves is an important parameter of the evaluation of a degree of their nutrition. Based on the content of elements in plant leaves, one may assess their amounts in fruits.

Quantitative dependence between the elemental content in leaves and fruits of various plants is the basis for evaluating the level of plant nutrition during its growth and development. In scientific literature data are published about relationships between concentrations of trace elements in vine leaves and berries (Fang, Zhu 2014, Milićević et al. 2018, Ricardo Rodrigues et al. 2019). Our research results indicate statistically significant relations between the content of almost all elements in leaves and berries (Table 3). The highest value of the correlation coefficient was observed in the case of Sr, Cu, Zn and As: 0.872, 0.734, 0.811 and 0.778, respectively. A slightly lower, statistically significant dependence was observed for Al, B, Ba and Pb. Regarding these elements, one can conclude that determination of their content in leaves may be an effective method of estimating the chemical composition of berries. The lowest values of the correlation coefficient between vine leaves and berries was found for calcium, chromium, lithium, magnesium, manganese, nickel and potassium (Table 3). The highest value of the correlation coefficient between the content of elements in soil and leaves was observed in the case of B, Ba, Sr, Cr, Na, P and As, while the strongest correlations between the elemental content in soil and fruit were determined for B, Fe, Ni, Sr, P, As (Table 3)

CONCLUSIONS

1. The analysed grapes were characterised by low K, P and Mg content.
2. High Cu, Fe, Ni, Pb, Cr and Al content was determined in the berries.
3. The content of potentially toxic elements never exceeded critical values for products intended for consumption in accordance with the FAO/WHO guidelines.
4. For the majority of the studied elements, statistically significant correlation coefficients between their content in vine leaves and berries were reported.
5. Higher values of the correlation coefficient between elemental content in soil and plants were found in the case of leaves than for berries.
6. In the case of Sr, Cu, Na, Cd, Zn, As, Al, B, Ba and Pb, statistically significant relationships between the content in leaves and berries were determined.

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