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Original scientific paper

DISTRIBUTION OF HEAVY METALS IN SOME VEGETABLES GROWN IN THE VICINITY OF LEAD AND ZINC SMELTER PLANT

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Gardens near the lead and zinc smelter plant "Zletovo" in the town of Veles, Republic of Macedonia, are the main suppliers with vegetables and fruits for the residents of this town. This area, was exposed thirty years to high environmental contamination with heavy metals (Cd, Pb and Zn). The smelter plant was a major source of heavy metals pollution in the environment, including the garden soils used for the production of vegetables and fruits. The aim of this study is to determine the level of contamination (especially with Cd, Pb and Zn) in green garlic (*Allium sativum*) and green onion (*Allium scallion*) produced on the contaminated soil and to determine its level of accumulation in the plants. The contents of 21 elements (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) in the vegetables and corresponding soils were analyzed by inductively coupled plasma – atomic emission spectrometry (ICP-AES) after microwave digestion. It was found that the contents of Cd, Pb and Zn in the vegetables from all of the four studied gardens is over the maximum permissible level according to the Macedonian regulations. The content of Cd in washed green garlic samples ranges from 0.60 to 2.70 mg kg^{-1}, for Pb from 4.30 to 6.14 mg kg^{-1} and for Zn from 11.7 to 29.9 mg kg^{-1}, while their contents in the washed green onion samples ranges from 0.77 to 2.66 mg kg^{-1} for Cd, from 3.98 to 5.35 mg kg^{-1} for Pb and from 21.2 to 38.0 mg kg^{-1} for Zn.

Key words: heavy metals; vegetables; green garlic; green onion; soils; metal accumulation

INTRODUCTION

The accumulation of heavy metals through the food chain, especially of Pb, Zn, Cd in soils and vegetables, may affect to the human health [1, 2]. Soil quality is one of the most important factors in sustaining the global biosphere. Heavy metals from polluted soils and water may accumulate in vegetables and thereby into enter to the human food chain [3–7].

Industrial activities and smelting operations from the smelter plant for lead and zinc "Zletovo" in Veles, Republic of Macedonia, is a major source of environmental pollution with heavy metals in the town and its environment [8–10]. This factory started to work officially in 1971 and was active until 2002. The pollution of the soil in the town of Veles and its environs was significantly increased as a result of 30 years of production from the smelter plant [11–13]. These polluted soils with heavy metals are still being used for production of food, mainly vegetables and fruits which can be a potential risk that affects the health of the population [14, 15]. The studies of this region show high contamination of topsoil especially with Cd, Pb, Zn, In, Hg, As and Sb, as a result of the pollution from the smelter plant [16–18].

The purpose of the present study is to determine the distribution of heavy metals in soils and vegetables (green onion and green garlic) produced in four gardens located in the vicinity of Pb-Zn smelter plant and to assess the level of accumulation of various elements. In order to explore the mobility and potential bioavailability of heavy metals, garden soils were tested using different extraction procedures.

EXPERIMENTAL

Study area

The town of Veles is located in the valley of the Vardar river, about 55 km south from the capital city of Skopje. The town Veles, for many of its characteristics and features, is a specific urban and industrial area. Its peculiarities originate both from its geographic location, since it is situated in the central part of Macedonia (Figure 1), and the economic and social character of its development. The urban area is located on 160–200 m of altitude, surrounded with hills from both sides of the valley, and with a height difference between 300 and 675 m. In 2002, 55000 inhabitants were registered in the municipality of Veles, while the town's population was 44000. The study area is large 1.5 km (W–E) × 3.5 km (N–S) and is located east from the river of Vardar with 5.25 km^2 cultivable land.

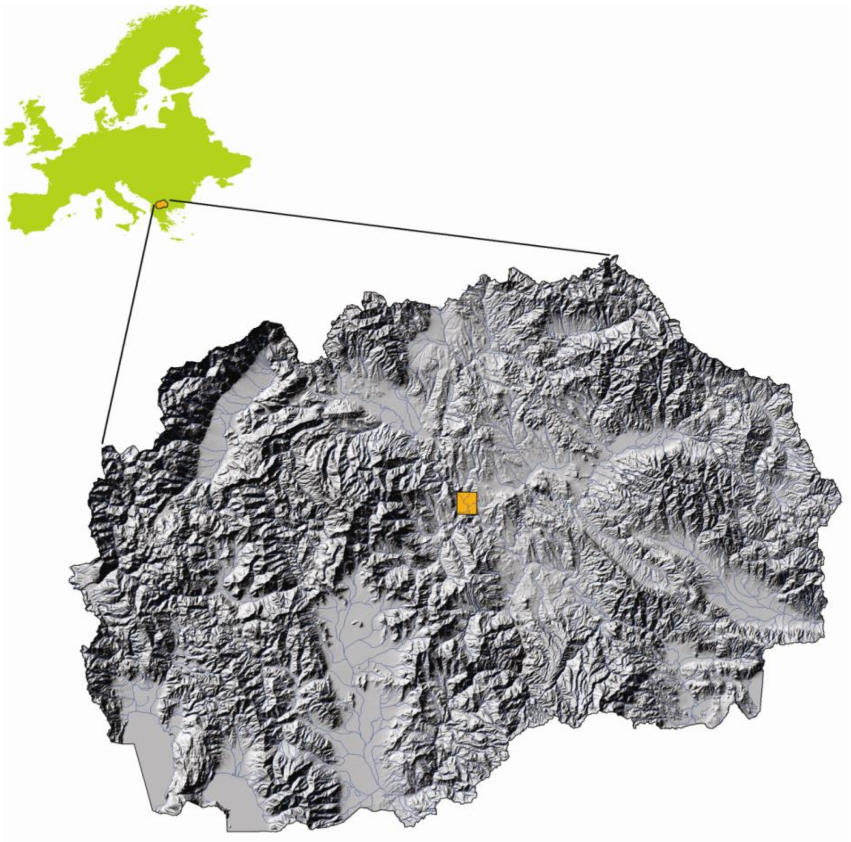

Figure 1. Study area

Sample collection and pre-treatment

From four different gardens in the area around the smelter plant nearby the town (Figure 2) soil samples and vegetables samples of green garlic (*Allium sativum*) and green onion (*Allium scallion*) were collected. For elements analysis, only the edible parts of vegetable samples were used. At each study site, soil samples (5–10 replicates) were taken from the rhizosphere of plant specimens. The eventually present organic fraction was excluded. Soil samples were air dried at room temperature about two weeks, and sieved through a 2 mm plastic sieve. The shifted mass was milled in agate mill to analytical grain size below 0.125 mm. The samples were stored in clean and dry plastic bags before the analysis.

Green garlic and green onion samples were chopped in small pieces and dried slowly, not directly to the sun. After drying samples were stored in clean and dry plastic bags before the analysis.

Procedure for digestion of soil and vegetable samples

The soil samples (0.25 g) were placed in a teflon digestion vessel and were digested on the asbestos net at hot plate at 100°C. Digestion was performed in three steps. In the first step, nitric acid was added to remove all organic matter, then a mixture of hydrofluoric acid and perchloric acid was added and in the third step hydrochloric acid (or nitric acid) and water was added to dissolve the residue. This solution was transferred quantitatively to the 25 ml volumetric flask.

The vegetable samples (0.50 g) were placed in a Teflon digestion vessels, 5 ml HNO_3 (69 %, *m*/*V*) were added, and the vessels were capped closed, tightened and placed in the microwave digestion system (Mars, CEM, USA). Plant samples were digested at 180 °C for 20 min, and after cooling down digested samples were quantitatively transferred to the 25 ml calibrated flasks.

Soil extractions

Three methods were applied for the investigation of plant-available elements: extraction in 0.1 mol l^{-1} HCl; extraction with H_2O and extraction of the soluble species of trace elements in a mixed buffered solution (pH=7.3) of triethanolamine (0.1 mol l^{-1}), calcium chloride (0.01 mol l^{-1}) and diethylenetriaminepentaacetic acid (DTPA, 0.005 mol l^{-1}) according to the ISO 14870 method. The extracts were filtered with a 0.45 μm filter and then analyzed for element concentrations. All reagents were of analytical grade, unless otherwise stated.

Instrumentation

All analyzed elements (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V and Zn) were determined by atomic emission spectrometry with inductively coupled plasma, ICP-AES (Varian, 715-ES) applying ultrasonic nebulizer CETAC (ICP/U-5000AT$^+$) for better sensitivity. Instrument parameters are given in the Table 1.

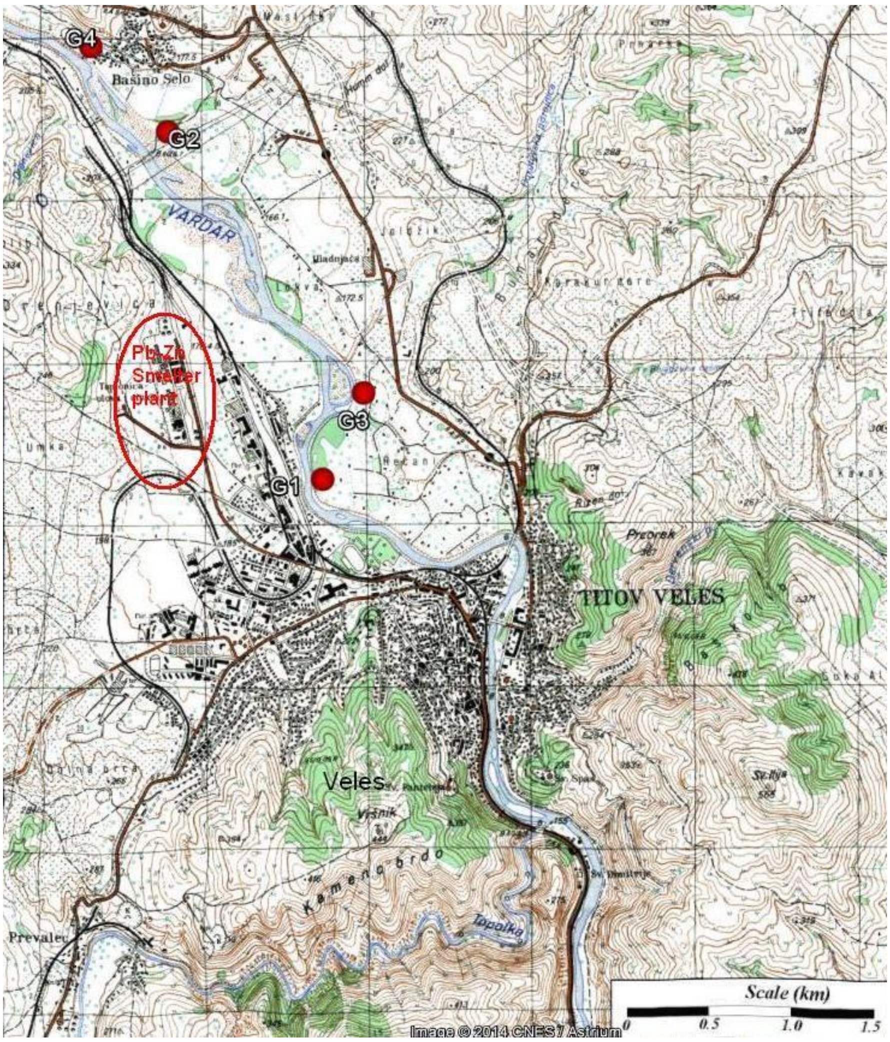

Figure 2. The map of the town of Veles with the garden locations (G1, G2, G3, G4)

Table 1. Instrumentation and operating conditions for ICP-AES system

RF generator					
Operating frequency	40.68 MHz free-running, air-cooled RF generator.				
Power output of RF generator	700–1700 W in 50 W increments				
Power output stability	Better than 0.1%				
Introduction area					
Sample nebulizer	Ultrasonic nebulizer CETAC (ICP/U-5000AT^{+})				
Spray chamber	Double-pass cyclone				
Peristaltic pump	0–50 rpm				
Plasma configuration	Radially viewed				
Spectrometer					
Optical arrangement	Echelle optical design				
Polychromator	400 mm focal length				
Echelle grating	94.74 lines/mm				
Polychromator purge	0.5 l min^{-1}				
Megapixel CCD detector	1.12 million pixels				
Wavelength coverage	177 nm to 785 nm				
Conditions for program					
RFG Power	1.0 kW	Pump speed	25 rpm		
Plasma Ar flow rate	15 l min^{-1}	Stabilization time	30 s		
Auxiliary Ar flow rate	1.5 l min^{-1}	Rinse time	30 s		
Nebulizer Ar flow rate	0.75 l min^{-1}	Sample delay	30 s		
Background correction	Fitted	Number of replicates	3		
Element	Wavelength, nm	Element	Wavelength, nm	Element	Wavelength, nm
Ag	328.068	Cu	324.754	Na	589.592
Al	396.152	Cr	267.716	Ni	231.604
As	188.980	Li	670.783	P	213.618
Ba	455.403	Fe	238.204	Pb	220.353
Ca	370.602	K	766.491	Sr	407.771
Cd	226.502	Mg	279.553	V	292.401
Co	238.892	Mn	257.610	Zn	213.857

The content of mercury in vegetable samples was determined by cold vapour atomic absorption spectrometer (SpectrAA 55B, Varian, USA) using a continuous flow vapour generation accessory (VGA-76, Varian, USA). The optimal instrumental parameters for this technique are given in Table 2.

Table 2. Instrumental parameters for CV-AAS

Instrument mode	Absorbance
Calibration mode	Concentration
Measurement mode	Integration
Wavelength	253.7 nm
Slit width	0.5 nm
Integration time	3 s
Delay time	40 s
Replicates	3
Sample flow rate	7 ml min^{-1}
Reaction media	HCl-$SnCl_2$
HCl flow rate	1 ml min^{-1}
$SnCl_2$ flow rate	1 ml min^{-1}

RESULTS AND DISCUSSION

Data from the analysis of 21 elements in the soil samples are presented in Table 3 and the contents of 22 elements in the plant samples (green garlic and onion) are given in Tables 4 and 5. Values of all elements are given in mg kg^{-1}.

Heavy metals content in soils

As a result of previous investigations conducted in the town of Veles and its surroundings, a high contamination of the topsoil was verified, especially with heavy metals which were produced from the Pb-Zn smelter plant situated near the town [16, 17]. However, the garden soils from this contaminated area were used for production of various vegetables. For that reason soils and vegetables produced in four different gardens near the smelter plant area (Figure 2) were used to determine the content of heavy metals in the soil and their accumulation in the edible parts of the investigated vegetables.

The pH of the soil samples was around pH 7.5. The heavy metals content in the studied soils resulted with high values for Pb, Zn and Cd. Thus, the content of cadmium in all four garden soils was over the target value of 0.8 mg kg^{-1} (Table 3). In the soil from the garden No. 1 the value for Cd was 6.77 mg kg^{-1} and in garden No. 3 the value for Cd was 6.64 mg kg^{-1} which was more than eight times higher than target value. In the garden No. 4 the value for Cd was 7.66 mg kg^{-1} which was more than nine times higher than target value and close to the intervention value (12 mg kg^{-1}). The lowest value 1.39 mg kg^{-1} for Cd was found in the soil from the garden No. 2 which was almost two times higher than the target values (0.8 mg kg^{-1}) for Cd.

Table 3. Contents of the analyzed elements in soils from four investigated gardens (in mg kg^{-1})

Element	Garden locations				Dutch list	
	1	**2**	**3**	**4**	Target	Intervention
Ag	0.24	0.32	0.67	0.79	–	–
Al	39550	34070	36250	40770	–	–
As	19.0	8.0	11.2	13.5	29	55
B	6.03	2.69	3.16	2.18	–	–
Ba	**350**	**750**	**304**	**291**	200	625
Ca	18800	24580	29960	43490	–	–
Cd	**6.77**	**1.39**	**6.64**	**7.66**	0.8	12
Cr	53.6	40.1	46.3	54.3	100	380
Cu	24.3	14.9	**41.1**	27.8	36	190
Fe	26400	16360	19080	18110	–	–
K	13860	16290	14160	12735	–	–
Li	17.9	19.7	19.5	14.4	–	–
Mg	9400	6075	7340	7140	–	–
Mn	537	408	503	585	–	–
Na	14620	11849	10090	9340	–	–
Ni	**36.2**	**35.8**	**40.7**	**58.1**	35	210
P	908	344	1192	1802		
Pb	**156**	46.0	**122**	**138**	85	530
Sr	170	99.7	121	148	–	–
V	96.3	37.8	55.5	41.7	–	–
Zn	**231**	65.3	**206**	**229**	140	720

The results for lead subsequently are: 156 mg kg^{-1}, 46 mg kg^{-1}, 122 mg kg^{-1} and 138 mg kg^{-1} in investigated garden soils (Table 3). When we compare the results for Pb (Table 3) with the values from Dutch National Standards for soil (the target value for lead was 85 mg kg^{-1} and intervention value was 530 mg kg^{-1}) it can be found that the content of Pb in three of the four studied garden's soil (Nos. 1, 3 and 4) was over the target value.

The values for Zn in the soils from the gardens Nos. 1, 3 and 4 (231 mg kg^{-1}, 206 mg kg^{-1}, 229 mg kg^{-1}, respectively) were also higher than the target value according to the Dutch standards (140 mg kg^{-1}). The content of Zn in the soil from the garden No. 2 was lower (65.3 mg kg^{-1}) that the target value.

The content of the other analyzed elements were bellow the limits given in the Dutch list. The exceptions were Ni and Ba which contents in soils from all gardens were over the referent values (35 mg kg^{-1} and 200 mg kg^{-1}, respectively). The content of Ba in the soil from the garden No. 2 was even over the intervention value (625 mg kg^{-1}). These high values for Ni and Ba (Table 3) resulted from their natural presence in the soil of this region [17, 18]. The content of Cu in the soil from the garden No. 3 which is very close to the smelter plant (Figure 2), was over the referent value (36 mg kg^{-1}, Table 3), and was a result of the pollution from the smelter plant [16–18].

Nutrients needed in large amounts by plants are referred to as macronutrients and include, phosphorus (P), potassium (K), calcium (Ca) and magnesium (Mg). Elements that plants need in trace amounts are called trace nutrients or micronutrients. Trace nutrients are not major components of plant tissue but are essential for growth. It was found that the contents of these elements in the investigated garden soils were in the range of the average of European soil [14]. Thus the content of phosphorous ranged from 344 to 1802 mg kg^{-1}, of K from 1.27 % to 1.63 %, of Ca from 1,88 % to 4,35 % and of Mg from 0.61 % to 0.94 %. The variation of the content of P depends mainly of the usage of phosphate fertilizers in different gardens while the content of the other macronutrients depends of the lithological background of the soil.

Heavy metals content in vegetables

The accumulation of metals in the edible parts of vegetables could have a direct impact on the health of nearby inhabitants, because vegetables produced from gardens are mostly consumed by the local population. Therefore, the content of metal contaminants in vegetables could be of concern to local residents. Leafy vegetables usually grow quickly and have high transpiration rates. This favors the uptake of metals by roots, and the resulting translocation of metals from roots to overground tissues. In addition, their broad leaves make these plants more susceptible to physical contamination by dust from soil and the splashing of rainwater [19].

The contents of Cd, Pb, Zn and other analyzed elements in the edible part of green garlic and green onion in washed and unwashed samples (expressed as content in dry samples), are given in Table 4 and Table 5 (for calculated fresh samples). The most important part of this study is to follow the contents of Cd, Pb and Zn in the vegetables. Their contents in both unwashed and washed green garlic and green onion were found to be very high. Thus, the content of Cd in the unwashed green garlic samples was in the range from 0.71 to 1.49 mg kg^{-1}, for Pb from 5.52 to 6.14 mg kg^{-1} and for Zn in the range from 12.9 to 37.2 mg kg^{-1} (expressed for dry samples) (Table 4, Figure 3). Comparing with the maximal permitted levels for Cd (0.3 mg kg^{-1} in dry samples and 0.05 mg kg^{-1} in fresh samples) and Pb (3 mg kg^{-1} in dry samples and 0.1 mg kg^{-1} in fresh samples) [20] it can be seen that the contents of Cd and Pb in most of the analyzed vegetables exceeded the food safety limit in the Repulic of Macedonia, with the average levels of Cd and Pb being 10 and 2.3 times that of the maximum permissible level, respectively (Tables 4 and 5, Figures 3 and 4).

The monitoring of the content of Cd, Pb and Zn was more important in the washed sample for this study, because people usually eat washed fresh vegetables or prepared in meal. Thus, the content of Cd in washed garlic sample was in the range from 0.60 to 2.70 mg kg^{-1}, for Pb from 4.30 to 6.14 mg kg^{-1} and for Zn from 11.7 to 29.3 mg kg^{-1} (Table 4, Figure 3) and the content of Cd in washed onion sample was in the range from 0.77 to 2.66 mg kg^{-1}, for Pb from 3.98 to 5,35 mg kg^{-1} and for Zn from 21.2 to 38,0 mg kg^{-1} (Table 4, Figure 3).

According to the water content in the analyzed vegetables, the contents in fresh samples were calculated (Table 5). The content of these heavy metals in fresh garlic and onion samples (both unwashed and washed) were very high compared to the national limits (Table 5, Figure 4). Thus, the content of Cd in the washed samples was in the range from 0.06 to 0.28 mg kg^{-1} (1.2–3 times higher than the permitted value), for Pb from 0.44 to 0.63 mg kg^{-1} (4.4–6.3 times over the limit) and for Zn from 1.19 to 3.05 mg kg^{-1}. It should also be emphasized the fact that the contents of these elements were not decreased significantly in the washed samples.

The obtained results from washed and unwashed samples of green garlic and green onion were compared with the maximum permissible levels according to the Macedonian regulations for food safety in fresh vegetables [20]. For the leafy vegetables the permitted level of Cd is 0.3 mg kg^{-1} (for dried samples) and 0.05 mg kg^{-1} (for fresh samples). The average content of Cd in the washed green garlic samples (0.17 mg kg^{-1}, calculated value for fresh samples) and in washed green onion samples (0.16 mg kg^{-1}) was about 3 times higher than the permitted level (Table 5).

Table 4. Contents of the analyzed elements in dry green garlic and onion from the investigated gardens (in mg kg^{-1})

	Green garlic					Green onion					
Garden	No. 1		No. 2		No. 3	No. 1		No. 2		No. 3	No. 4
Element	Washed	Unwashed	Washed	Unwashed	Washed	Washed	Unwashed	Washed	Unwashed	Washed	Washed
Al	18.5	17.0	15.5	58.3	11.5	13.0	10.3	50.8	211	10.5	28.3
As	0.25	0.55	<0.10	<0.10	<0.10	0.25	0.27	<0.10	0.30	<0.10	<0.10
Ba	6.44	5.51	9.44	9.95	14.3	9.14	10.4	6.60	17.5	6.90	1.31
Ca	3070	3100	4870	6420	7900	9360	10180	5360	5720	11400	11200
Cd	**1.16**	**1.49**	**0.60**	**0.71**	**2.70**	**0.77**	**0.94**	**2.13**	**2.18**	**2.66**	**0.92**
Co	0.10	0.13	0.02	0.01	0.03	0.07	0.04	0.03	0.12	0.07	0.05
Cr	0.26	0.33	0.27	0.37	0.25	0.24	0.19	0.56	1.03	0.17	0.25
Cu	3.96	4.08	6.80	14.4	4.40	5.68	5.90	4.81	6.52	5.23	3.51
Fe	53.0	87.5	48.2	99.5	34.4	40.0	27.5	117	307	31.4	64.5
Hg	0.002	0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
K	15980	16500	13840	16130	18990	7470	11400	19540	22140	13600	11030
Li	0.03	0.04	0.03	0.04	0.54	0.03	0.03	0.06	0.16	0.83	0.03
Mg	2080	2260	2830	3018	3050	3400	3430	3480	4130	4130	2530
Mn	5.57	5.82	7.37	10.2	7.67	13.1	8.68	20.3	23.8	30.5	9.57
Mo	0.13	0.20	0.62	0.66	<0.01	0.11	0.33	0.10	0.10	0.14	<0.01
Na	196	194	160	227	1070	464	654	1100	5060	27.0	585
Ni	0.51	0.36	1.55	1.58	0.54	0.76	0.73	1.28	1.07	0.70	1.01
P	3090	3440	1880	1804	3230	1590	1405	2190	1910	1290	2180
Pb	**4.30**	**5.52**	**5.31**	**6.14**	**6.14**	**3.98**	**4.35**	**4.55**	**6.89**	**4.54**	**5.35**
Sr	14.9	14.3	15.5	17.9	50.6	35.0	39.6	16.4	18.1	69.2	3.50
V	0.03	0.04	0.02	0.10	0.01	0.01	0.01	0.12	0.67	0.01	0.06
Zn	**29.3**	**37.2**	**11.7**	**12.9**	**29.9**	**28.0**	**25.4**	**36.7**	**35.1**	**38.0**	**21.2**

Table 5. Contents of the analyzed elements in fresh green garlic and green onion from the investigated gardens (in mg kg^{-1})

	Green garlic					Green onion					
Garden	No. 1		No. 2		No. 3	No. 1		No. 2		No. 3	No. 4
Element	Washed	Unwashed	Washed	Unwashed	Washed	Washed	Unwashed	Washed	Unwashed	Washed	Washed
Al	1.73	1.89	1.58	5.95	1.18	1.01	1.28	4.98	20.6	1.03	2.77
As	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Ba	0.56	0.66	0.96	1.01	1.46	1.02	0.89	0.65	1.71	0.68	0.13
Ca	317	313	496	655	805	998	918	525	561	1117	110
Cd	**0.12**	**0.15**	**0.06**	**0.07**	**0.28**	**0.09**	**0.08**	**0.21**	**0.21**	**0.26**	**0.09**
Co	0.013	0.010	0.002	0.001	0.003	0.004	0.007	0.003	0.012	0.007	0.005
Cr	0.034	0.027	0.028	0.038	0.26	0.019	0.024	0.05	0.10	0.017	0.025
Cu	0.42	0.40	0.69	1.47	0.45	0.58	0.56	0.47	0.64	0.51	0.34
Fe	8.93	5.41	4.92	10.1	3.51	2.69	3.92	11.5	30.1	3.08	6.32
Hg	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
K	1680	1630	1412	1645	1937	1117	732	1915	2170	1333	1081
Li	0.003	0.004	0.003	0.004	0.06	0.003	0.003	0.006	0.016	0.08	0.003
Mg	230	213	289	308	311	336	333	341	405	405	248
Mn	0.59	0.57	0.75	1.04	0.78	0.85	1.29	1.99	2.34	2.99	0.94
Mo	0.02	0.01	0.06	0.07	<0.01	0.01	0.03	0.01	<0.01	0.01	<0.01
Na	19.8	20.0	16.3	23.2	109	64.1	45.5	108	496	2.65	57.3
Ni	0.04	0.05	0.16	0.16	0.06	0.07	0.07	0.13	0.10	0.69	0.10
P	351	315	192	184	330	138	155	215	187	127	214
Pb	**0.44**	**0.56**	**0.54**	**0.63**	**0.63**	**0.39**	**0.43**	**0.45**	**0.68**	**0.44**	**0.52**
Sr	1.46	1.52	1.58	1.83	5.16	3.88	3.43	1.61	1.77	6.78	0.34
V	0.004	0.003	0.002	0.01	0.001	0.001	0.001	0.012	0.066	0.001	0.006
Zn	**2.99**	**3.79**	**1.19**	**1.32**	**3.05**	**2.49**	**2.74**	**3.44**	**3.60**	**3.72**	**2.08**

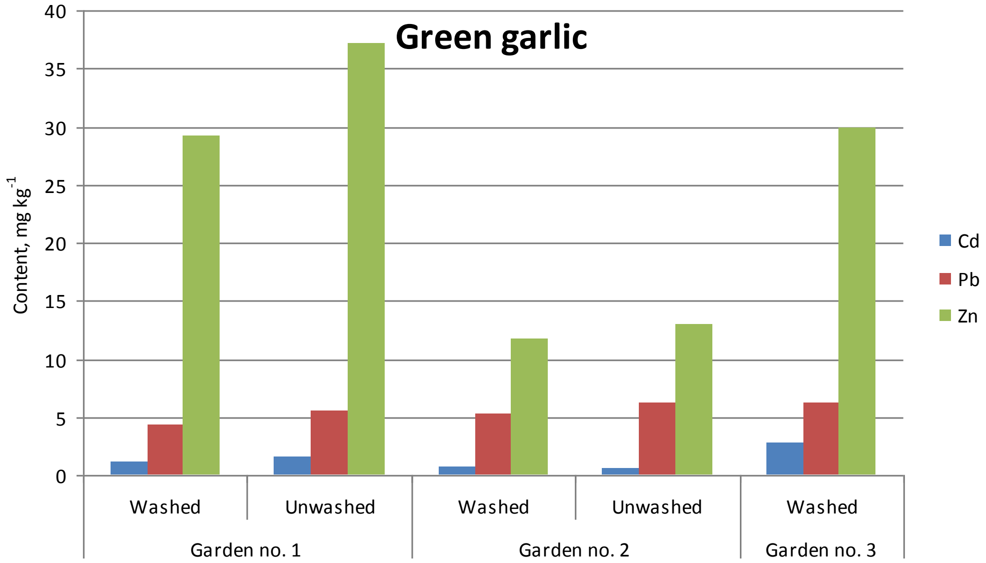

Figure 3. Content of Cd, Pb and Zn in dry (washed and unwashed) green garlic from three different gardens

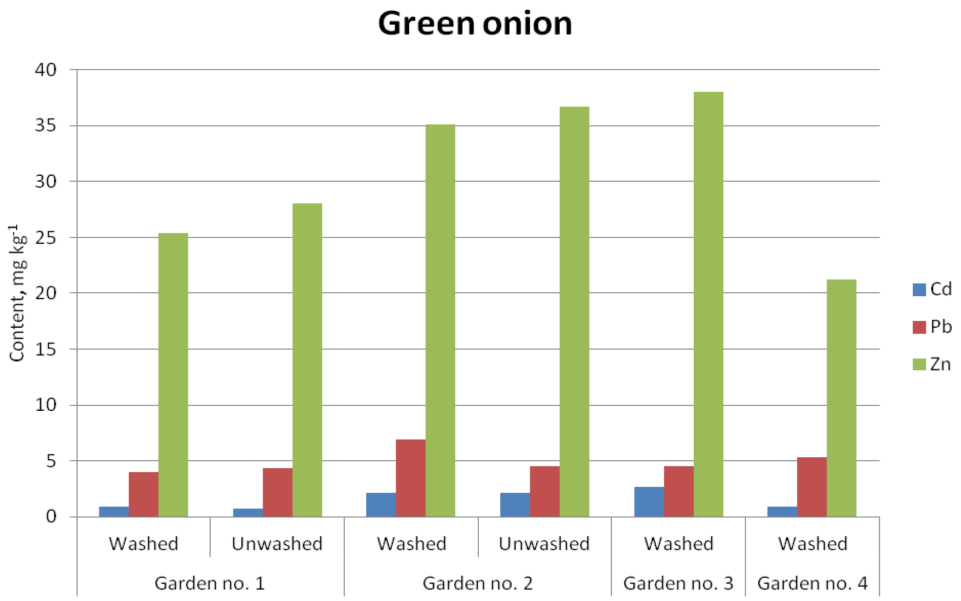

Figure 4. Contents of Cd, Pb and Zn in dry (washed and unwashed) green onion from four different gardens

According to the Macedonian regulations for food safety in fresh vegetables, the permitted level for Pb in the leafy vegetables is 0.1 mg kg^{-1}. We can note that the content of Pb in the washed samples of green garlic (0.58 mg kg^{-1}) was 5.8 times higher while in the unwashed green garlic samples (0.54 mg kg^{-1}) it was 5.4 times higher than the limit. The main source for this additional influence was the emission from the waste Pb-Zn-Cd smelter slag deposit situated in the near vicinity. Very similar results were obtained for green onion.

This results show that the local inhabitants are exposed to heavy metals contamination, as a result of consuming the vegetables that grow in the Veles area. These data for the presence of Cd and Pb even at very low concentration, warn of serious health effects on people [21]. Considering all these data it can be concluded that there are indications of serious health risks, caused by Cd and Pb in vegetables consumed by the population of Veles.

For the rest of the analyzed elements (Tables 3–5) it can be concluded that there was no statistically significant correlation between their content in all washed and unwashed samples of green garlic and onion samples.

Extraction capacity of Cd, Pb and Zn

A major concern in this area is the fact that on such contaminated soils the local population is still cultivating vegetables. The pH of soil has a great role in the bio-availability of heavy metals. In the present study, the pH of the four examined soils ranged between 7.4 and 7.8. Different vegetable species have different cumulative capacities of heavy metals. Also, different heavy metals have different behavior and different enrichment capacities. With calculation of enrichment coefficients we may present the contamination in soil and vegetables around the Pb-Zn smelter.

The amount of heavy metals uptake by the vegetable samples depends on the presence of these elements in the garden soil, their solubility, physico-chemical properties of the soil, plant species and age, as well as on exposure time [22]. Different degrees of availability can be estimated depending on the extracting power of the reagent that is used.

For that reason, extraction for plant-available elements of soil samples were performed in H_2O, 0.1 mol l^{-1} HCl and by buffered DTPA-$CaCl_2$-TEA solutions. Extraction with water provides the information on the actual availability of elements from the soil solution. Extraction with acid reagents was often used to displace potentially available forms that were not easily extracted. Hydrochloric acid was used to extract some forms of Cu, Ni, Zn, Cd, Pb or Hg [23]. Extraction with mixed reagents was also widely used for selective solubilization by chelate formation, often in combination with other reagents acting by ion exchange, redox or acid action. The most widely used mixed reagents were used for the estimate of the extraction of trace elements with DTPA solution. This standard uses the reagent DTPA-$CaCl_2$-TEA, which was also recommended for extraction of toxic metals.

The extraction level of Cd, Pb and Zn in H_2O, 0.1 mol l^{-1} HCl and DTPA-$CaCl_2$-TEA solution from the garden soils collected from the locations where vegetable species were taken are given in Figures 5–7. From Figure 5 it can be seen that the most available element from all four garden soil samples in H_2O extracts, was Zn. Thus, in the garden soil from the locations of Nos. 1 and 2, the amount of 0.2 mg kg^{-1} and 0.08 mg kg^{-1} of Zn was extracted which represented from 0.08 % to 0.12 % of the Zn present in the soil. Lower levels of Zn were extracted from the garden soils from the locations No. 3 and No. 4 (0.045 to 0.047 mg kg^{-1}, or 0.04 % extractability). The extraction for Pb from the soil samples collected from the location No. 2 was the highest (0.03 mg kg^{-1}; extractability 0.06 %); while from the soils collected from locations No. 3 and No. 4 the contents were lower (0.042 mg kg^{-1} and 0.035 mg kg^{-1}; extractability 0.034 % and 0.026 %). Obviously the extraction for Cd with H_2O is much higher in the soil samples from location No. 2 and No. 3 (extractability 0.11 % and 0.039 %), than in the samples from locations No. 1 and No. 4.

In extraction solution of 0.1 mol l^{-1} HCl from soils where vegetable samples were taken, the extractability of Cd was the highest; the extracted amounts of Cd varied from 0.03 mg kg^{-1} (0.53 % extractability) to 0.005 mg kg^{-1} (0.17 % extractability). The values for Pb and Zn were very similar.

From Figure 7 it can be seen that the extractability of Cd, Pb and Zn was the highest in the extraction solution of DTPA-$CaCl_2$-TEA. Thus, in soil collected from the location of No. 3, the amount of 1.11 mg kg^{-1} of Cd was extracted which represented about 16.7 % of the Cd present in the soil. While, from the soils from the locations No. 1 and No. 4 smaller amounts of Cd were extracted (15.7 % and 15.4 %, respectively). In the soil from the location No. 2 extracted amount of Cd was 10.28 %.

This high extractability of Cd in the DTPA, explains the high amounts of this element in the vegetable samples.

CONCLUSION

The intensive uncontrolled processing of pollution in the past has resulted in the release of large amounts of heavy metals in the local environment, and caused high concentrations of metals to be present in the surrounding soils and water. Vegetables grown in the nearby sites were also contaminated with heavy metals, especially with Cd and Pb, which could be a potential health risk to local inhabitants. The pollution from the past now may act now as a source of pollution for the surrounding area, due to the extremely high concentrations of heavy metals in the affected soils. A long-term risk assessment needs to be carried out on the leach ability and migration potential of these toxic elements at the contaminated sites.

The aim of this study was to assess the influence of soil contamination caused by the 30 years work of the Pb-Zn smelter plant in the city of Veles, Republic of Macedonia, and its influence on the pollution with heavy metals of vegetables produced in this area.

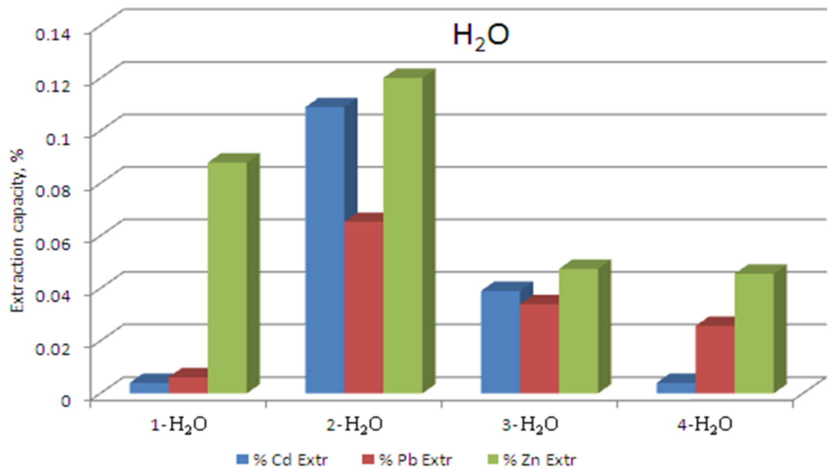

Figure 5. Extraction for plant-available Cd, Pb and Zn in H_2O extraction solution from soils where vegetable species were taken

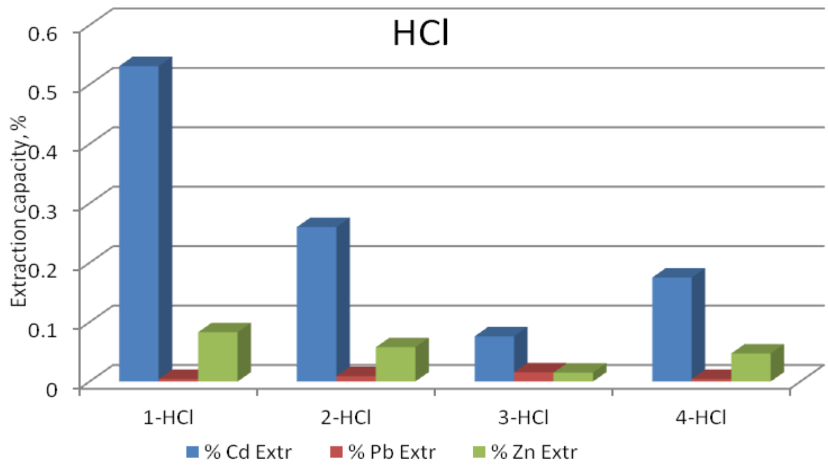

Figure 6. Extraction for plant-available Cd, Pb and Zn in extraction solution of 0.1 mol l^{-1} HCl from soils where vegetable species were taken

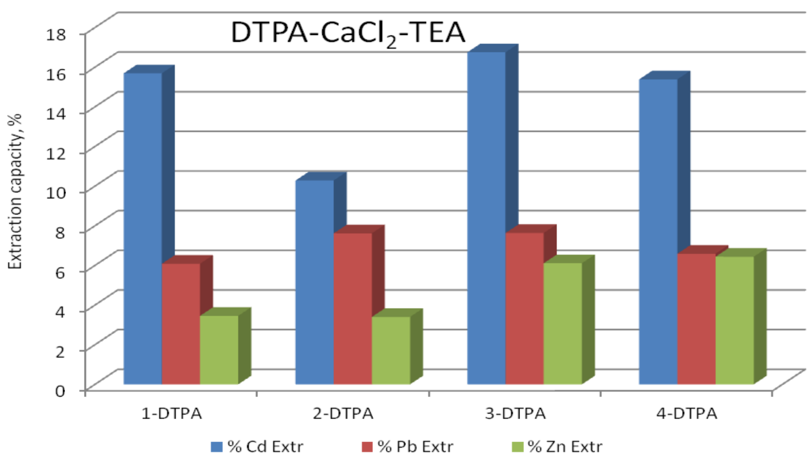

Figure 7. Extraction for plant-available Cd, Pb and Zn in extraction of buffered DTPA-$CaCl_2$-TEA solution from soils where vegetable species were taken

It was found that the levels of heavy metals in soils from the studied gardens exceeded the target values according to the Dutch standards. Thus the content of Cd was up to 10 times higher than the maximum permitted concentrations of Cd in the soils, the levels of Pb were about 2–3 times higher, indicating that the soils in this area are unsuitable for food production. The bioavailability of Cd was the highest in the extraction solutions of 0.1 mol l^{-1} HCl and DTPA-$CaCl_2$-TEA, while in H_2O the most extractable were Zn and Cd. The highest extraction capacity for Pb, Cd and Zn was distinguished in the extraction solution of DTPA-$CaCl_2$-TEA. The order of heavy metals extractability from the analyzed garden soils in buffered DTPA solution was: Cd>Pb>Zn, for Cd<16 %, for Pb<10 % and for Zn<7.9 %. The obtained high extractability of these elements shows that if these elements are present in high content in the garden soils they can be easily accumulated in the vegetables cultivated on these soils.

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ДИСТРИБУЦИЈА НА ТЕШКИ МЕТАЛИ ВО НЕКОИ ЗЕЛЕНЧУЦИ ПРОИЗВЕДЕНИ ВО БЛИЗИНА НА ТОПИЛНИЦА ЗА ОЛОВО И ЦИНК

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Земјоделските површини кои се во близина на топилницата за олово и цинк „Злетово“ во градот Велес, Република Македонија, се единствени површини за производство на зеленчук и овошје за жителите на градот Велес. Оваа област триесет години е изложена на загадување со тешки метали (Cd, Pb и Zn). Топилницата претставува главен извор на загадување на животната средина со тешки метали, вклучувајќи ги и земјоделските почви кои се користат за производство на зеленчук и овошје. Главна цел на ова испитување е да се определи нивото на загадување (посебно со Cd, Pb и Zn) во млад лук (*Allium sativum*) и млад кромид (*Allium scallion*) кои се произведени на загадените почви и да се определи нивото на акумулацијата на овие елементи во растенијата. По подготовката на примероците од зеленчук и почвата тие беа растворени и потоа анализирани со примена на атомска емисиона спектрометрија со индуктивно спрегната плазма (ИСП-АЕС). Притоа е определена содржината на 21 елемент (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, V и Zn). Утврдено е дека содржината на Cd, Pb и Zn во зеленчукот е над максимално дозволените граници според регулативата во Република Македонија. Содржината на Cd во измиените примероци од млад лук се движи од 0,60 до 2,70 mg kg^{-1}, на Pb од 4,30 до 6,14 mg kg^{-1} и на Zn од 11,7 до 29,9 mg kg^{-1}, додека содржините во миените примероци од млад кромид тие се движат од 0,77 до 2,66 mg kg^{-1} за Cd, од 3,98 до 5,35 mg kg^{-1} за Pb и од 21,2 до 38,0 mg kg^{-1} за Zn.

Клучни зборови: тешки метали; зеленчук; млад лук; млад кромид; почви; акумулација на метали