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Distribution of Heavy Metals in Lettuce and Carrot Grown in the Vicinity of Lead and Zinc Smelter Plant

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ABSTRACT: Soils near Pb-Zn smelter plant "Zletovo" situated in the town of Veles, Republic of Macedonia, are exposed to high environmental contamination related to heavy metal pollution (Cd, Pb and Zn) from waste disposal sites. In this city a Pb-Zn smelter plant was a major source for heavy metals pollution of the environment, including the agriculture land used for the production of vegetables and fruits. The goal of this study is to assess the level of contamination with heavy metals (with particular focus on Cd, Pb and Zn) of lettuce and carrot that grow on contaminated soil and to determine its level of accumulation in plant tissues. Samples of different parts of the plants and corresponding soils were processed, digested and then analyzed by inductively coupled plasma – atomic emission spectrometry (ICP-AES). It was found that the content of Cd, Pb and Zn in vegetables exceeded the maximum permissible concentration. The content of Cd in washed lettuce samples was in the range from 1.72 to 2.58 mg kg^{-1}, for Pb from 2.11 to 5.57 mg kg^{-1} and for Zn from 21.8 to 37.5 mg kg^{-1}. The content of these elements in the washed carrot samples for Cd was in the range from 1.19 to 2.16 mg kg^{-1}, for Pb from 5.04 to 7.14 mg kg^{-1} and for Zn from 13.9 to 23.8 mg kg^{-1}.

Keyword: heavy metals, metal accumulation, vegetables, lettuce, carrot, soil, Veles area

INTRODUCTION

Industrial activities, mining and smelting operations, are recognized as the main sources of metal pollution of soils [1-4]. Heavy metals contamination of agricultural soils and crops in the vicinity of mining and industrial areas has been regarded as a great environmental concern [5-7]. The threat that heavy metals pretense to human and animal health is aggravated by their long-term persistence in the environment [8]. Excessive accumulation of heavy metals in agricultural soils around industrial activities and mining areas, resulting in elevated heavy metal uptake by food crops, and is a great concern because is potential health risk to the local inhabitants [9-11]. Cultivation of crops for human or livestock consumption on contaminated soil can potentially lead to the uptake and accumulation of heavy metals in the edible plant parts with a resulting risk to human and animal health [12, 13]. It is known that serious systemic health problems can develop as a result of excessive dietary accumulation of heavy metals such as Cd, and Pb in the human body [14]. Vegetables take up metals by absorbing them from contaminated soils, as well as from deposits on different parts of the vegetables exposed to the air from polluted environments [15]. Food contamination by heavy metals depends on their mobility in the soil and their bioavailability.

However, there are cases when the industrial enterprises, especially mining and metallurgical plants, situated near cities may increase the pollution. From recently published articles, Pb-Zn smelter plants lead to enormous soil contamination [11, 16-18]. There were several studies in the past on the presence of heavy metals in soil and vegetables and fruits produced near the city of Veles, Republic of Macedonia [19-21]. Namely, in this city a lead and zinc smelter plant "Zletovo", active until 2002, was a major source for heavy metals pollution of the environment. Our recent study conducted in this region shows high contamination of topsoil especially with Cd, Pb, Zn, In, Hg, As, Sb, as a result of pollution from the smelter plant [22-24]. However, even at present

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time the agriculture land in this area is used for production of vegetables and fruits. To determine their potential for metal accumulation, vegetables (lettuce and carrot) that grow on contaminated soil were investigated in this study.

For this purpose in the present study the content of 22 major and trace elements in the soil and vegetables from the gardens that were affected by the Pb and Zn smelter plant around the town of Veles was determined. Focus has been given on the accumulation of Pb, Zn and Cd in relation to their mobility in lettuce and carrot. To assess the level of accumulation of various elements, the samples of lettuce and carrot produced from three gardens from the contaminated areas were collected. In order to explore the mobility and potential bioavailability of heavy metals, garden soils were tested using different extraction procedures.

MATERIALS AND METHODS

Study area

The city of Veles is located in the valley of the Vardar River, about 55 km south from the capital town Skopje. The town Veles, for many of its characteristics and features, is a specific urban and industrial area. Its peculiarities originate from both, its geographic location, since it is situated in the centre of Macedonia (Fig. 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. The area of present-day Veles has been inhabited for over a millennium. In 2002, 55000 inhabitants were registered in the municipality of Veles, while the town´s population was 44000.

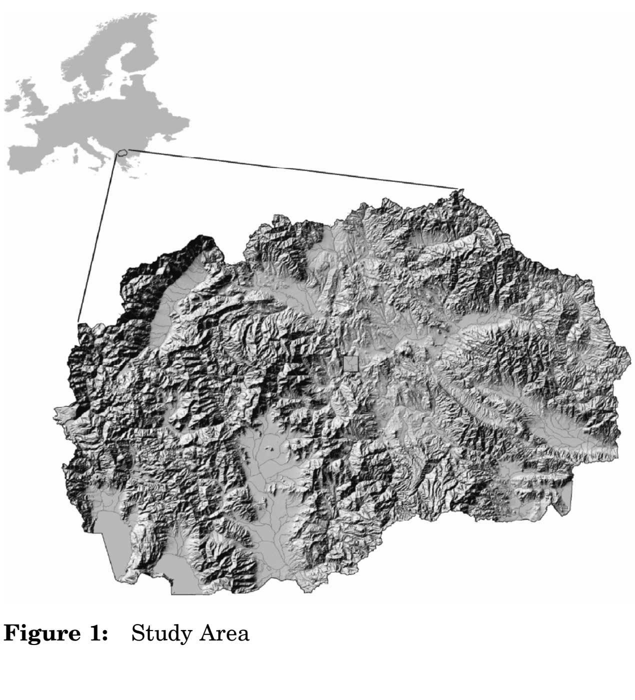

Figure 1: Study Area

Sample Collection and Pre-treatment

From three different gardens in the area around the smelter plant nearby the town (Fig. 2) soil samples and vegetables samples of lettuce (*Lactuca sativa*) and carrot (*Daucus carota*) 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 passed through a 2 mm plastic sieve. The shifted mass was milled in agate mill to analytical grain size below 0.125 mm. The sample was stored in clean and dry plastic bag before the analysis.

Lettuce and carrot 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.

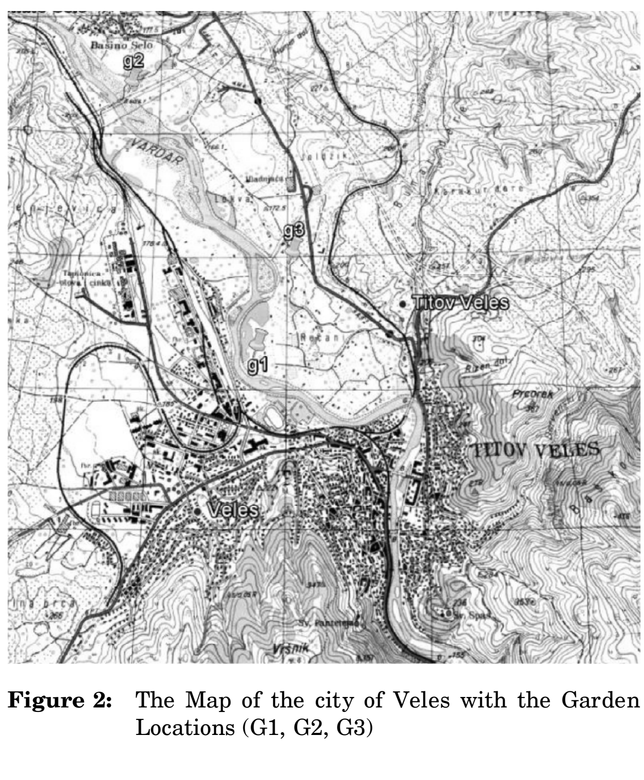

Figure 2: The Map of the city of Veles with the Garden Locations (G1, G2, G3)

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 M 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.

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 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

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 including heavy metals were presented in Table 3 and the values of 22 elements in the plant samples (lettuce and carrot) were given in Table 4 and 5. Values of all elements were given in mg kg^{-1}.

Heavy Metals Content in Soils

As a result of previously investigations that were conducted in the town Veles and its surroundings, it was verified a high contamination of the topsoil, especially with heavy metals which were produced from the Pb-Zn-Cd smelter plant situated near the town [23, 24]. However, from this contaminated area the garden soils were used for production of vegetables and fruits. For that reason soils and vegetables produced in three different gardens in the smelter plant area (Fig. 2) were used to determine the content of heavy metals in the soil and their accumulation in the crops.

The pH of the soil samples was around pH 7 (Table 3). The heavy metals content in the studied soils resulted with high values for Pb, Zn and Cd.

The content for Pb was 122 mg kg^{-1}, 156 mg kg^{-1} and 189 mg kg^{-1} for each garden, 206 mg kg^{-1}, 231 mg kg^{1} and 284 mg kg^{-1} for Zn and 6.64 mg kg^{-1}, 6.77 mg kg^{-1} and 8.72 mg kg^{-1} for Cd. If we compare the results for Pb (Table 3) with the values from Dutch National Standards (*http://www.contaminatedland.co.uk/std-guid/dutch-l.htm*) 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 the studied garden's soil was over the target value. Significantly higher values for Zn in the garden soil from the garden No. 3 were also observed (284 mg kg^{-1}) which were higher for 2.0 times than the target value according to the Dutch standards (140 mg kg^{-1}). The content of Zn in the soil from the two other garden were also higher than the target value.

The content of cadmium in all three garden soils was over the target value of 0.8 mg kg^{-1} (Table 3). The highest value for Cd was in the soil from the garden N° 3 (8.72 mg kg^{-1}) which was ten times higher than the target values (0.8 mg kg^{-1}) for Cd. In the soil from the garden No. 1 it was 6.77 mg kg^{-1} and in garden No. 2 was 6.64 mg kg^{-1} which was more than eight times higher than target value and close to the intervention value (12 mg kg^{-1}).

Heavy Metal Content in Vegetables

The content of Cd, Pb, Zn and other analyzed elements in the edible part of lettuce and carrot produced in these gardens (washed and unwashed samples) are given in Table 4 and 5. The most significant elements for this study are Cd, Pb and Zn. Their contents in both unwashed and washed lettuce and carrot were very high. The contents of Cd in the unwashed lettuce samples were in the range from 3.06 to 4.0 mg kg^{-1}, of Pb from 5.47 to 10.0 mg kg^{-1} and for Zn in the range from 30.12 to 50.2 mg kg^{-1}.

Table 3
Content of the Analyzed Elements in Soil from three Investigated Gardens (in mg kg^{-1})

Element	*Garden locations*			*Dutch List*	
	1	*2*	*3*	*Target*	*Intervention*
pH	7.69	7.54	7.35		
Ag	0.24	0.67	0.63	-	-
Al	39553	36248	32794	-	-
As	19.0	11.2	12.3	29	55
B	6.03	3.16	4.56	-	-
Ba	350	304	313	**200**	**625**
Ca	18800	29961	15799	-	-
Cd	6.77	6.64	8.72	**0.8**	**12**
Cr	53.6	46.3	47.7	100	380
Cu	**24.3**	41.1	37.4	**36**	**190**
Fe	26397	19081	24193	-	-
K	13856	14163	12700	-	-
Li	17.9	19.5	16.7	-	-
Mg	9399	7336	8874	-	-
Mn	537	503	527	-	-
Na	14618	10090	13677	-	-
Ni	**36.2**	40.7	40.4	**35**	**210**
P	908	1192	903		
Pb	156	122	189	**85**	**530**
Sr	170.4	121	136	-	-
V	96.3	55.5	73.1	-	-
Zn	231	206	284	**140**	**720**

The content of Cd, Pb and Zn was more important and curious for the washed sample in this study (Table 4, Fig. 3). Thus, the content of Cd in washed lettuce sample was in the range from 1.72 to 2.58 mg kg^{-1}, for Pb from 2.11 to 5.57 mg kg^{-1} and for Zn from 21.8 to 37.5 mg kg^{-1}.

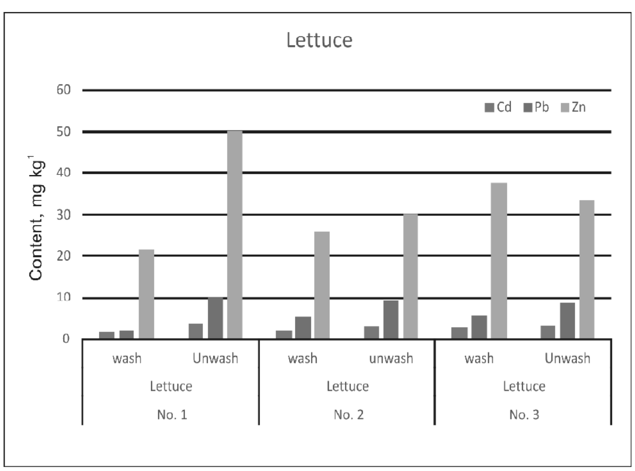

Figure 3: Content of Cd, Pb and Zn in dry (washed and unwashed) lettuce from three different gardens

The content of these heavy metals in carrot samples were also very high (Table 4, Fig. 4). The content of Cd in unwashed sample was in the range from 1.58 to 2.44 mg kg^{-1}, for Pb from 6.61 to 10.36 mg kg^{-1} and for Zn from 15.1 to 22.8 mg kg^{-1}. However, it was found that the content of these elements were not decreased significantly in the washed samples and the content of Cd was in the range from 1.19 to 2.16 mg kg^{-1}, for Pb from 5.04 to 7.14 mg kg^{-1} and for Zn from 13.9 to 23.8 mg kg^{-1} (Fig. 4).

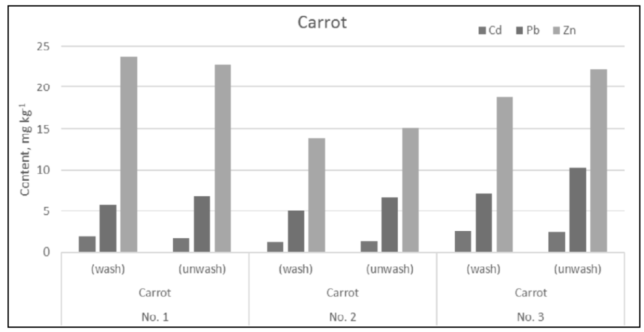

Figure 4: Content of Cd, Pb and Zn in Dry Wash and Unwashed Carrot from three Different Gardens

From the obtained results for the lettuce and carrot samples it was concluded that the highest content was found for Zn in all unwashed samples (Figs. 3 and 4). It can be also concluded that there is not significant difference between washed and unwashed samples especially for the carrot samples. However, the differences in the content for washed and unwashed samples of lettuce were obvious. It was comprehensible for lettuce to except that beside the extraction of heavy metals from the soil to have also dust deposition as an additional influence in the contamination, unlike the carrot that the heavy metals were extracted by the roots from the soil.

The obtained results from washed and unwashed samples of lettuce and carrot were compared with the maximum permissible level according to the Macedonian regulations for food safety in fresh vegetables [25]. The limited levels for Cd in fresh vegetable for stemmed and root vegetables is 0.1 mg kg^{-1} and if we compare the average value for Cd from the washed samples of carrot (0.32 mg kg^{-1}) it can be seen that the content of Cd in the edible part of the carrot is 3.2 times higher than the permitted levels for Cd in fresh vegetable. The unwashed samples for carrot are not so different from the washed samples (average

Table 4
Content of the Analyzed Elements in Dry Lettuce and Carrot from three Investigated Gardens (in mg kg^{-1})

Garden soil	Lettuce *No. 1*		Lettuce *No. 2*		Lettuce *No. 3*		Carrot *No. 1*		Carrot *No. 2*		Carrot *No. 3*	
Element	*Washed*	*Unwashed*	*Washed*	*Unwashed*	*Washed*	*Unwashed*	*Washed*	*Unwashed*	*Washed*	*Unwashed*	*Washed*	*Unwashed*
Al	5.61	720	31.7	589	103	625	47	180	26.4	121	122	439
As	0.43	0.21	0.49	0.17	0.31	0.06	0.25	0.31	0.48	0.22	0.57	0.43
Ba	5.20	14.3	12.0	13.8	7.40	10.5	13.2	10.9	7.61	11.8	13.3	16.2
Ca	7792	15226	3822	5394	14635	16368	3007	2922	3214	3109	3462	3900
Cd	1.72	4.00	2.22	3.06	2.58	3.25	1.96	1.58	1.19	1.28	2.61	2.44
Co	0.06	0.21	0.03	0.25	0.19	0.28	0.13	0.16	0.02	0.05	0.08	0.27
Cr	0.35	2.28	0.29	1.83	0.55	1.52	0.32	0.6	0.26	0.45	0.68	1.45
Cu	6.26	10.3	5.24	14.7	12.9	20.8	8.15	6.29	4.85	4.68	7.2	6.74
Fe	80.6	625	41.0	513	159	657	63.9	1914	55.6	147	181	564
Hg	0.016	0.005	<0.001	<0.001	<0.001	0.001	0.0006	<0.001	<0.001	<0.001	0.001	<0.001
K	12844	26061	27323	28143	22042	22910	12067	9411	18688	15697	27676	21574
Li	0.07	0.46	0.37	0.58	0.14	0.42	0.04	0.12	0.03	0.08	0.09	0.29
Mg	3768	5228	4094	5012	4452	4724	3288	2813	3268	2834	3331	3500
Mn	9.95	30.8	8.03	28.4	41.0	54.4	10.2	12.3	7.42	11.2	10.2	19.8
Mo	0.27	0.39	-	0.14	0.36	0.30	0.1	-	0.03	0.03	0.18	-
Na	1275	2344	9084	9627	4263	4938	6647	6395	1885	2873	4846	6640
Ni	1.99	3.15	0.67	1.03	1.67	4.19	1.92	1.59	0.65	0.76	1.42	1.99
P	1540	2520	1752	2180	2840	2787	1714	1412	1773	1887	1509	1184
Pb	2.11	10.0	5.47	9.33	5.57	8.51	5.76	6.78	5.04	6.61	7.14	10.3
Sr	22.7	45.0	34.9	38.8	29.4	33.1	12	11.9	13.4	12.6	19.3	21.6
V	0.08	1.76	0.04	1.05	0.25	1.63	0.12	0.5	0.1	0.32	0.36	1.41
Zn	21.8	50.2	26.1	30.1	37.5	33.2	23.8	22.8	13.9	15.1	18.9	22.3

Table 5
Content of the Analyzed Elements in Fresh Lettuce and Carrot from three Investigated Gardens (in mg kg^{-1})

	Lettuce						*Carrot*					
Garden	*No. 1*		*No. 2*		*No. 3*		*No. 1*		*No. 2*		*No. 3*	
Elem.	*Washed*	*Unwashed*	*Washed*	*Unwashed*	*Washed*	*Unwashed*	*Washed*	*Unwashed*	*Washed*	*Unwashed*	*Washed*	*Unwashed*
Al	0.30	37.9	5.43	32.9	1.67	31.0	7.89	30.2	20.5	73.7	4.43	20.3
As	0.02	0.01	0.02	0.00	0.03	0.01	0.04	0.05	0.10	0.07	0.08	0.04
Ba	0.27	0.75	0.39	0.55	0.63	0.73	2.22	1.83	2.23	2.72	1.28	1.98
Ca	410	802	771	862	201	284	505	491	581	655	540	522
Cd	0.09	0.21	0.14	0.17	0.12	0.16	0.33	0.27	0.44	0.41	0.20	0.21
Co	<0.001	0.01	0.01	0.01	<0.001	0.01	0.02	0.03	0.01	0.05	<0.001	0.01
Cr	0.02	0.12	0.03	0.08	0.02	0.10	0.05	0.10	0.11	0.24	0.04	0.08
Cu	0.33	0.54	0.68	1.10	0.28	0.77	1.37	1.06	1.21	1.13	0.81	0.79
Fe	4.25	32.9	8.38	34.6	2.16	27.0	10.7	321	30.4	94.7	9.33	24.7
Hg	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
K	677	1373	1161	1207	1439	1483	2026	1580	4647	3622	3137	2635
Li	<0.001	0.02	0.01	0.02	0.02	0.03	0.01	0.02	0.02	0.05	0.01	0.01
Mg	198	275	235	249	216	264	552	472	559	588	549	476
Mn	0.52	1.62	2.16	2.87	0.42	1.50	1.71	2.06	1.71	3.32	1.25	1.88
Mo	0.01	0.02	0.02	0.02	-	0.01	0.02	-	0.03	-	0.01	0.01
Na	67	123	225	260	479	507	1116	1074	814	1115	316	482
Ni	0.10	0.17	0.09	0.22	0.04	0.05	0.32	0.27	0.24	0.33	0.11	0.13
P	81	133	150	147	92	115	288	237	253	199	298	317
Pb	0.11	0.53	0.29	0.45	0.29	0.49	0.97	1.14	1.20	1.73	0.85	1.11
Sr	1.20	2.37	1.55	1.74	1.84	2.04	2.01	2.00	3.24	3.63	2.25	2.12
V	<0.001	0.09	0.01	0.09	<0.001	0.06	0.02	0.08	0.06	0.24	0.02	0.05
Zn	1.15	2.64	1.98	1.75	1.37	1.59	4.00	3.83	3.17	3.74	2.33	2.53

value of 0.29 mg kg^{-1}). For the leafy vegetables regulations for the permitted level of Cd is 0.2 mg kg^{-1}. The content of Cd in the washed lettuce samples (0.114 mg kg^{-1}) is less than in unwashed lettuce samples (0.181 mg kg^{-1}) (Table 5), because dust deposition has an additional influence in the contamination with these toxic elements. Thus, the permitted levels for Pb in the leafy vegetables is 0.3 mg kg^{-1} we can see that in washed samples of lettuce (0.23 mg kg^{-1}) the content of Pb is in the permitted values but for unwashed lettuce samples (0.49 mg kg^{-1}) is 1.6 times higher. The dust deposition from the waste deposit of smelter slag is the source for this additional influence. The regulations for the permitted levels for Pb in fresh stemmed and root vegetables are 0.1 mg kg^{-1}. For the obtained values for the content of Pb in washed samples of carrot (1.0 mg kg^{-1}) we can see that the content of Pb in the carrot is 10 times higher than the permitted levels for Pb in fresh carrot. Thus, for the unwashed samples of carrot (1.33 mg kg^{-1}) the content of Pb is similar as those in washed samples. The same conclusion could be obtained for the content of Zn. Namely, its content in washed (3.16 mg kg^{-1}) and unwashed (3.37 mg kg^{-1}) samples of carrot and washed lettuce (1.5 mg kg^{-1}) and unwashed lettuce (1.99 mg kg^{-1}) (Table 5) is similar.

The obtained results from the dry samples of lettuce and carrot were compared with the maximum permissible level regulations for food safety in dry vegetables [26]. Thus, the limited level for Cd in dry vegetable is 0.3 mg kg^{-1} and if we compare the average value for Cd from the washed samples of lettuce (2.45 mg kg^{-1}) we can see that this value is more than 8.0 times higher than the permitted level. The average value for Pb in washed samples from lettuce was 4.38 mg kg^{-1} and it was over limited values of 3.0 mg kg^{-1}. The range for lead in carrot was 5.04 to 7.14 mg kg^{-1} and it was two times higher than the permitted level. This means that the local inhabitants were exposed to heavy metal contamination consuming vegetables that grow in the Veles area. Cd and Pb are nonessential elements and their presence even at very low concentration causes adverse health effects to human health [27]. The present results indicate that there is a serious potential health risk associated with Cd and Pb in vegetables that threatens inhabitants in the vicinity 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 carrot and lettuce samples. In general, the content of the rest of the heavy metals are bellow that maximal permitted levels.

Extraction Capacity of Cd, Pb and Zn

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 to present the contamination in soil and vegetables around the Pb-Zn smelter.

The intensity of heavy metals uptake by the vegetable samples depends on the presence of these elements in the garden soil, solubility, physico-chemical properties of the soil, plant species and age, as well as on exposure time [28]. Assay of large number of elements, does not always provide sufficient information about the availability for plants of nutritive elements in the soil. Different degrees of availability can be estimated depending on the extracting power of the reagent that is used.

The data about the plant-availability of some heavy metals from the soil the extraction tests of soil samples collected from gardens should be performed. For that reason, extraction for plant-available elements of soil samples were performed in H_2O, 0.1 M HCl and by buffered DTPA-$CaCl_2$-TEA solution. *Extraction with water* only provides information on the actual availability of elements from the soil solution. Many different reagents were available for extraction by ion-exchange in buffered or not buffered mediums [29]. *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 [30]. *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 including DTPA action. This standard uses the reagent DTPA-$CaCl_2$-TEA, which was also recommended for extraction of toxic metals [30].

The extraction level of Cd, Pb and Zn in H_2O, 0.1 M HCl and DTPA-$CaCl_2$-TEA solution from the garden soil collected from locations where vegetable species were taken was given in Figs. 5-7. From Fig. 5 we can see that the most available element from all three garden soil samples in H_2O extracts was Zn. Thus, in the garden soil from the locations of No. 1 and 3, the amount of 0.2 mg kg^{-1} and 0.24 mg kg^{-1} of Zn was extracted which represented about 0.08% of the Zn present in the soil. Lower levels of Zn were extracted from the garden soil from the location No. 2 (0.09 mg kg^{-1}, or 0.04 % extractability).

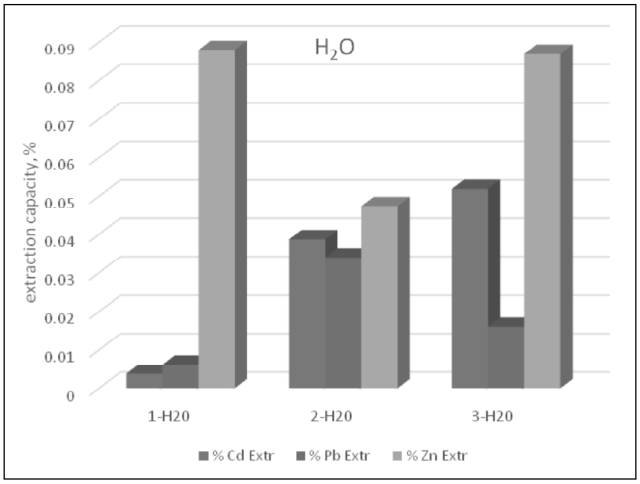

Figure 5: Extraction for plant-available Cd, Pb and Zn in H_2O extraction solution from soil where vegetable species were taken

In extraction solution of 0.1 M HCl from soil where vegetable species were taken, the extractability of Cd was the highest varying of the extracted amounts of Cd from 0.005 mg kg^{-1} (0.07% extractability) to 0.12 mg kg^{-1} (1.38% extractability).

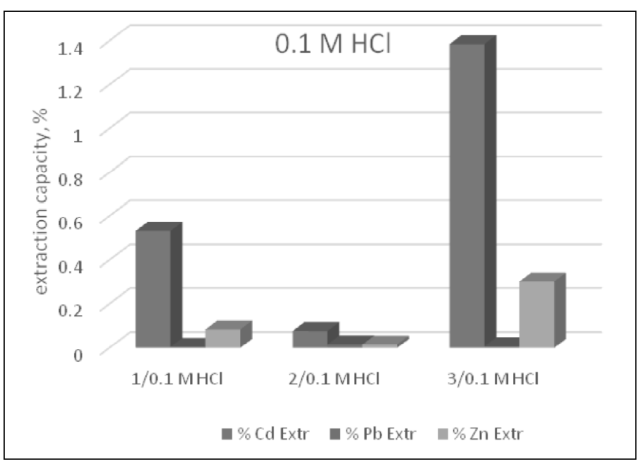

Figure 6: Extraction for plant-available Cd, Pb and Zn in extraction solution of 0.1 M HCl from soil where vegetable species were taken

From Fig. 7 it can be seen that the extractability of Cd, Pb and Zn in extraction solution of DTPA–$CaCl_2$–TEA was the highest for all elements from the soils from all three locations. Thus, in soil from the locations of No. 3, the amount of 2.4 mg kg^{-1} of Cd was extracted which represented about 27.7% of the Cd present in the soil, while, from the soils from the location No. 2 and No. 1 smaller amount for Cd was extracted (16.7 % and 15.6 %, respectively). This high extractability of Cd in the DTPA extract explain high amounts of these elements in the vegetable samples.

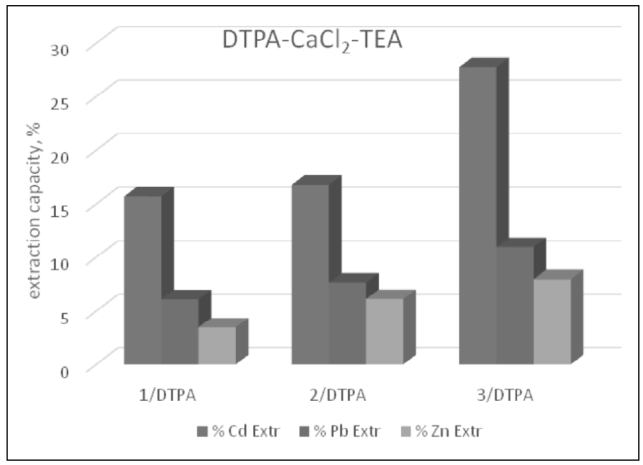

Figure 7: Extraction for plant-available Cd, Pb and Zn in extraction of buffered DTPA-$CaCl_2$-TEA solution from soil where vegetable species were taken

CONCLUSION

The aim of this study was to assess the influence of soil contamination from 30 years work of Pb-Zn smelter plant in the city of Veles, Republic of Macedonia, and it's influence to the pollution with heavy metals of vegetables produced at this area. 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 10 time higher than the maximum permitted concentrations of Cd in the soils, the levels of Pb and Zn was two time higher, indicating that the soils in this area is unsuitable for agricultural use. Different vegetable species have different capacities to accumulate heavy metals, and different heavy metals have different enrichment coefficients in the vegetables. Extraction order of heavy metals from the analyzed garden soils in buffered DTPA solution as follows: Cd>Pb>Zn, for Cd <27%, for Pb <10% and for Zn <7.9%. The obtained high extractability of these elements allows its high content in the vegetables produced on this land. Thus, the content of Cd, Pb and Zn were several times higher in carrot and lettuce produced in the investigated area compared with the permissible values.

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