



Distribution of heavy metals in the garden soil and vegetables grown in the vicinity of lead and zinc smelter plant

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Abstract Veles town was exposed on the 30 years pollution with heavy metals from the lead and zinc smelter plant. The aim of this study is the exploration of distribution of Cd, Pb and Zn as well as some other elements in soil and vegetables from the gardens around the town. In total 42 samples from different vegetable products (crops and green mass) from 5 gardens were investigated. It was found that the content of Cd, Pb and Zn in vegetables exceeded the maximum permissible concentration. The content of Cd ranges from 0.55 mg kg⁻¹ in beetroot to 5.56 mg kg⁻¹ in pepper-leaf. Average value for Cd for all 42 vegetable samples (washed and unwashed) is 1.64 mg kg⁻¹. All this three values are over maximal permitted limit (MPL) of 0.3 mg kg⁻¹ for Cd in dry vegetable. The content of Pb ranges from 3.67 mg kg⁻¹ in daicon-leaf to the maximal value of 32.4 mgkg⁻¹ in celery with average value for Pb of 6.87 mg kg⁻¹ exceeding the MPL of 3.0 mg kg⁻¹ in all vegetable samples. Also, the presence of zinc is in high range from 18.6 to 67.0 mg kg⁻¹, with 34.36 mg kg⁻¹ average value.

Keywords heavy metals, soils, vegetables, enrichment coefficient, food safety

Introduction

Exploitation and consumption of energy and mineral resources by the man causes pollution on the air and biosphere with different chemical elements [1]. Soils contain chemical elements of various origin: lithogenic elements which are directly inherited from the lithosphere, pedogenic elements which are of lithogenic origin, but their concentration and distribution in soil layers and soil particles are changed due to the pedogenic processes, or anthropogenic elements which are all those deposited into soil as direct or indirect results of human activities. For this reason, urban pollution with heavy metals has recently become a subject of many studies [2-4]. The regional contamination of soil occurs mainly in industrial regions and within centres of large settlements where factories, motor vehicles and municipal wastes are the most important sources of heavy metals. The natural background itself is variable, which means that higher concentrations of some elements can be considered normal for one region but abnormal for another. However, there are cases when the industrial enterprises, especially mining and metallurgical plants, situated near cities can increase the pollution. From articles published in recently years, lead and zinc mines and smelter plant lead to enormous soil contamination [5-8]. 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 [9]. The accumulation through the food chain of heavy metals, especially Pb, Zn or Cd in soils and vegetables may ultimately affect to the human health. Soil quality is one of the most important factors in sustaining the global biosphere. It has been defined in several different ways in recent years from the view points of productivity, sustainability, environmental protection, and human health. Heavy metals from polluted soils and air may accumulate in vegetable and thereby enter to the human food chain. Smelter for lead and zinc „Zletovo” in the town of Veles is a major source for enrichment concentration of heavy metals in Veles and its environment. This



factory, official starts with work in 1971 year and was active until 2002 year. For those 30 years the pollution of the soil around the town was remarkably increased.

There were several investigations of air, soil, vegetables and fruits produced in the region of Veles [10-17]. The recent studies conducted in this region show high contamination of topsoil especially with Cd, Pb, Zn, In, Hg, As, Sb, as a result of pollution from the smelter plant [16, 17]. However, even at present time the agriculture land in this area is used for production of vegetables and fruits. To determine their potential for metal accumulation, vegetables that grow on contaminated soil were examined in this study.

The enrichment content of As, Cd, Cu, Pb, Sb and Zn in the soil from the studied gardens is a results of the human activity and all this chemical elements are present by anthropogenic activities [15-17]. This polluted soils, until today are used for producing a food like vegetable and fruit which is potential source with affect to people's health. For this purpose in the present study the content of 22 major and trace elements in the soil and vegetables were determined from the gardens that were affected by the Pb and Zn of the smelter plant in Veles. Focus has been given on the accumulation of Pb, Zn and Cd in relation to their mobility in vegetables. To assess the level of accumulation of various elements, the samples of vegetables produced from five 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 town of Veles is located in the valley of the Vardar river, about 55 km south from the capital Skopje. Veles, for many of its characteristics and features, is a specific urban and industrial area. Its peculiarities originate from both its geographic location (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. In 2002, 55000 inhabitants were registered in the municipality of Veles, while the town's population was 44000. The garden area is large: 3.7 (W-E) x 1.3 (S-N) km (Fig. 2) and is located in the north-east part of Veles and study area occupies 4.8 km².

Samples of the soils and vegetables were collected from five different locations from the area around the smelter „Zletovo” near by town Veles (Fig. 2). The locations of the gardens are on different distances from the Pb-Zn smelter „Zletovo” in Veles, Macedonia. Fourteen different vegetables (leak, beetroot, daikon, parsley, radish, celery, white icicle, potato, green pepper, aubergine, collard greens, parsnip, broccoli and tomato) were collected and analyzed, to compare their uptake and accumulation of heavy metals. The vegetable 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. 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 sample was stored in clean and dry plastic bag before the analysis.

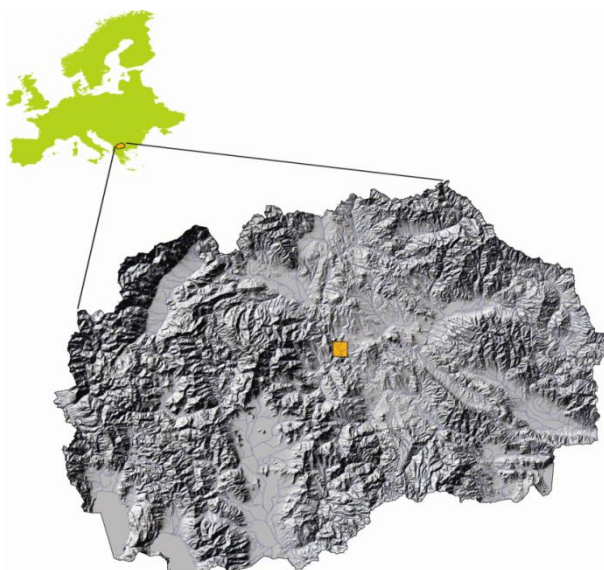


Figure 1: Study area



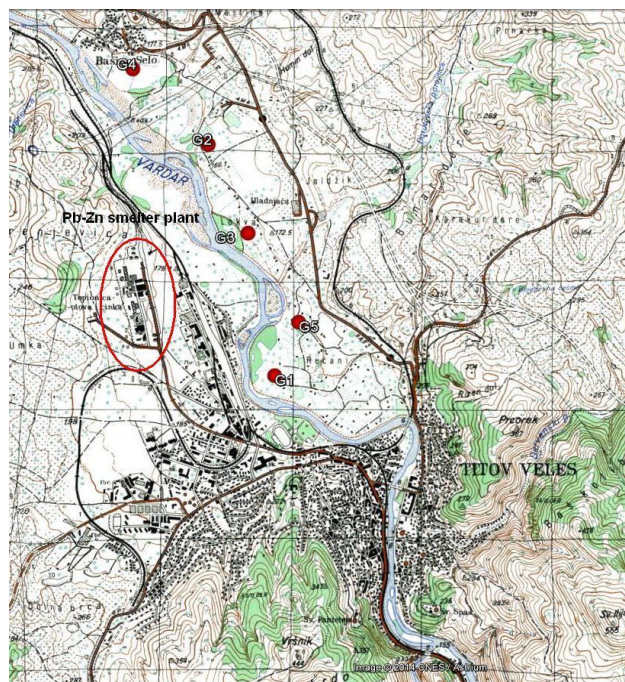


Figure 2: Location of the gardens

Procedure for digestion of soil and plant samples

The soil samples (0.25 g) were placed in a Teflon digestion vessel and were digested on the asbestos net plate 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, and then a mixture of HF and HClO₄ is added and in the third step HCl and water were added to dissolve the residue. This solution was transferred quantitatively to the 25 ml volumetric flask.

Dry plant samples (0.50 g) were placed in a Teflon digestion vessels, 5 ml HNO₃ (69%, *m/v*) were added, and the vessels were capped closed, tightened and placed in the rotor of the Mars microwave digestion (CEM, USA). Plant samples were digested at 180°C. After cooling the digested samples were quantitatively transferred to the 25 ml calibrated flasks.

Soil extractions

Three methods were applied for the examination of plant-available elements: extraction in 0.1 mol l⁻¹ HCl; extraction with H₂O 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, diluted with bidistilled water into 25 ml calibrated flasks 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 the application of atomic emission spectrometry with inductively coupled plasma, ICP-AES (Varian, 715-ES) applying ultrasonic nebulizer CETAC (ICP /U-5000AT⁺) for better sensitivity. For this study, certified materials were used to validate the method for all considered elements and the difference between measured and certified values was satisfied ranging within 15%. The theoretical limit for (ICP-AES) methods is in ppb (μg l⁻¹) range for the majority of elements. For some elements, values between ppb and ppm levels were further examined using more complex quantitative methods. 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).

Results and Discussion

Analysis of soils and vegetables

As a result of previous study conducted in the town of Veles and its surroundings, it was verified a high contamination of the topsoil, 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 five different gardens near the smelter plant area (Fig. 2) were used to determine the content of heavy metals in the soil and their accumulation in the edible parts of the investigated vegetables. Data from the analysis of 21 elements in soil samples collected from the studied gardens are presented in Table 1. It could be noticed that the content of heavy metals (Cd, Pb, Zn) which are present in soil is very high and it is due to the Pb-Zn smelter plant activities. The pH of the soil samples is in the range from 7.35 to 7.98 and is varied from neutral to moderately alkaline. Content of Cd in soil from the examined area is in the range from 1.39 mg kg⁻¹ to 8.72 mg kg⁻¹ and the average value for Cd is 6.24 mg kg⁻¹. Target value for Cd by Dutch Standards for Soil Environmental Quality is 0.8 mg kg⁻¹ (Table 1). Value for Cd in all five garden soils are over the target value, 8-10 times over in soil from the gardens No. 1 (6.77 mg kg⁻¹), No. 2 (8.72 mg kg⁻¹), No. 4 (7.66 mg kg⁻¹) and No. 5 (6.64 mg kg⁻¹), and almost two times over in soil from garden No. 3 (1.39 mg kg⁻¹). None results are not close or over the intervention value of 12 mg kg⁻¹ for cadmium (Table 1).

Target value for Pb by Dutch Standards for Soil Environmental Quality is 85.0 mg kg⁻¹ (Table 1). The content of Pb in this examined area is in the range from 46.0 mg kg⁻¹ to 189 mg kg⁻¹ and the average value for Pb is 130 mg kg⁻¹. In four gardens soil the value for Pb is two times over the (Table 1), only in garden soil No. 3 (46 mg kg⁻¹) is under target value. All five results for Pb are under intervention value of 530 mg kg⁻¹ by Dutch Standards for Soil Environmental Quality. The content of Zn in these samples from five garden soils is in the range from 65.3 mg kg⁻¹ to 284 mg kg⁻¹ and the average value for Zn is 203 mg kg⁻¹. One value of 65.3 from garden No. 3 is under the target value of 140 mg kg⁻¹ (Table 1). The other values for Zn of 231 mg kg⁻¹, 284.00 mg kg⁻¹, 228.8 mg kg⁻¹ and 206 mg kg⁻¹ are over the target value (140 mg kg⁻¹) but not closely to the intervention value (720 mg kg⁻¹) (Table 1).

The content of the other analyzed elements are below the limits given in the Dutch list. The exceptions are Ni, Ba and V for which the contents in soil from all gardens are over the referent values (35 mg kg⁻¹, 160 mg kg⁻¹ and 42 mg kg⁻¹, respectively). The content of Ba in soil from garden No. 3 is even over the intervention value (625 mg kg⁻¹). These high values for Ni, Ba and V (Table 1) are as a result of their natural presence in soil from this region [15-17]. The content of Cu in soil from garden No. 3 which is very close to the smelter plant (Fig. 2), is over the referent value (36 mg kg⁻¹, Table 1), and is a result of the pollution from the smelter plant [17].

Table 1: Content of the analyzed elements in soil from 5 investigated gardens (results given in mg kg⁻¹)

Element	Garden locations					The New Dutch standard values	
	1	2	3	4	5	Target	Intervention
pH	7.69	7.35	7.98	7.48	7.54		
Ag	0.24	0.63	0.32	0.79	0.67	-	15
Al	39550	32790	34070	40770	36250		
As	19.0	12.3	8.00	13.5	11.2	29.0	55.0
B	6.03	4.56	2.69	2.18	3.16		
Ba	350	313	750	291	304	160	625
Ca	18800	15800	24580	43490	29960		
Cd	6.77	8.72	1.39	7.66	6.64	0.8	12
Cr	53.6	47.7	40.1	54.3	46.3	100	380
Cu	24.3	37.4	14.9	27.8	41.1	36.0	190
Fe	26400	24190	16360	18110	19080		
K	13860	12700	16290	12735	14160		
Li	17.9	16.70	19.7	14.4	19.5		
Mg	9400	8870	6075	7140	7340		
Mn	537	527	408	585	503		
Na	14620	13680	11850	9340	10090		
Ni	36.2	40.4	35.6	58.1	40.7	35.0	210
P	908	903	344	1802	1192		
Pb	156	189	46.0	138	122	85.0	530
Sr	170	137	99.7	148	121		
V	96.3	73.1	37.8	41.7	55.5	42.0	250
Zn	231	284	65.3	229	206	140	720



Heavy metals content in different vegetables

The high content of these heavy metals in soil from the gardens leads to their very high content in the vegetables produced on such polluted soil. Different vegetable species have different cumulative capacities of heavy metals. Also, different heavy metals have different behavior and different enrichment capacities [18]. With calculation of enrichment coefficients we may present the pollution in soil and vegetables around the Pb-Zn smelter plant. Therefore, the high content of metal contaminants in vegetables could be a concern to local residents.

The contents for 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) in the 42 samples of edible parts from different vegetables are listed in Table 2 where the content of the elements in both washed and unwashed vegetables is also given.

The content of Pb, Zn and Cd are more interesting for this study due to the present soil pollution (Table 1) from the Pb-Zn smelter plant [17]. The content of Cd in dry vegetable samples (Table 1) is in the range from 0.19 mg kg⁻¹ in broccoli (garden No. 3) to 5.6 mg kg⁻¹ in pepper leaf (garden No. 4) and the average value from all analysed vegetables for Cd is 1.64 mg kg⁻¹. Almost all values for Cd are over the Maximal Permitted Level (MPL) according to national legislation of 0.3 mg kg⁻¹ (Table 2) [19, 20]. Maximum content is almost 20 times higher than MPL. Lead in dry vegetable is in the range from 3.67 mg kg⁻¹ in daicon-leaf (Garden No. 1) to 32.4 mg kg⁻¹ in celery (garden No. 3) with an average value from all analysed vegetables for Pb is 6.87 mg kg⁻¹ 2.29 times higher than the MPL of 3 mg kg⁻¹ in dry vegetables And the maximal value is more than 10 times higher than the MPL (Table 2).

Zinc is not limited according to the legislation but still its content is high and in correlation with the content of Cd and Pb. Thus the minimal value was found in potato sample from the garden No. 4 (18.6 mg kg⁻¹), the maximal content of 67.0 mg kg⁻¹ was found in celery sample from garden No. 3. Observing the gardens it can be seen that the highest values for these elements are found in the vegetables from the gardens No. 2 and 3 (Table 2). Comparing the content of these elements in soil it is obvious that the reason for such high content is not only the soil pollution but also their location which is very close to the smelter plant and the slag deposit which is the source of air pollution by the powdered slag rich in these elements [17]. This is also confirmed by the significantly higher values in the leaves of vegetables (Table 2).

As for the vegetables themselves it is evident that washing only partially reduces the content of heavy metals which means that they are accumulated within the fruit. This in turn indicates the ability of most of these vegetables to absorb heavy metals from the soil. From the other analysed elements only arsenic and mercury are regulated by national legislation. The results given in Table 2 shows that in almost all analyzed samples the content of these two elements is below the maximum allowable content. The exceptions are the samples of celery and white icecicle leaf from garden No. 3.

Assimilation by vegetables

Accumulation of elements from soil by plants has been studied in a wide range of plant species [21-23] but the relationship between heavy metals in the soil and plant uptake is still not well understood. Almost all of plant species have been found that accumulate large quantities of Cd, Pb and Zn when present in the area around the Pb-Zn smelter in Veles [16, 17]. Plant heavy metals uptake 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 [24] Assay of large number 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. *Extraction with water* only provides information on the actual availability of elements from the soil solution. Many different reagents are available for extraction by ion-exchange in buffered or not buffered mediums [25]. *Extraction with acid reagents* is often used to displace potentially available forms that are not easily extracted. Hydrochloric acid is used as 0.1 mol L⁻¹ to extract some forms of Cu, Ni, Zn, Cd, Pb or Hg [26]. *Extraction with mixed reagents* is 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 are used for the estimate of the extraction of trace elements including DTPA action. This standard uses the reagent DTPA-CaCl₂-TEA, which is also recommended for extraction of toxic metals [26].

With the simulation of these extractions we can obtain a conclusion about the plant-available elements and conditions that live plants in this area are exposed to large amounts of Cd, Pb and Zn present in the soil. For that reason, extraction for plant-available elements of soil samples were performed in H₂O, in 0.1 mol L⁻¹ HCl and by buffered DTPA-CaCl₂-TEA solution. The level of extraction of Cd, Pb and Zn from the soil samples collected from locations where vegetable species were taken is given on Figs. 3-5.

The extractable value for cadmium is under detection limit in the water medium in all five soil samples from gardens No. 1 to 5 (Fig. 3). Content of extractible Cd in water (Fig. 3) for the soil samples from the gardens No. 1 and No. 5 is in the range of 0.005 to 0.0003 mg kg⁻¹. However it is about 10 times higher for the extracts of the



soil samples from the gardens No. 2, 3 and 4 (range of 0.0015 to 0.0045 mg kg⁻¹). The content of extractible zinc in water extract (Fig. 3) is similar for all gardens soil (in the range of 0.0078 mg kg⁻¹ to 0.247 mg kg⁻¹ with slightly higher extractability of the soil from the gardens No. 1 and 2. Lead is less extractable from the soil samples from location No. 1 then from the locations No. 2, 3, 4 and 5 (Fig. 3). The content of extractible lead in water (Fig. 3) for location No. 1 is 0.010 mg kg⁻¹, and content of extractible lead for locations No. 2-5 is in the range of 0.030 to 0.042 mg kg⁻¹.

Table 2a: The content of the analyzed elements in vegetable samples taken from the 5 location (given in mg kg⁻¹ dry mass)

Vegetable	Garden No.	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K
Aubergine	4	19.1	0.41	0.55	657	2.98	0.03	0.33	3.67	53.9	0.001	20956
Beetroot (w)	1	19.7	0.60	13.7	1200	0.62	0.12	0.29	8.53	58.3	0.001	18275
Beetroot (unw)	1	98.4	0.55	12.9	956	0.55	0.12	0.44	8.63	154	0.001	19368
Beetroot leaf (w)	1	28.4	0.62	49.6	15711	3.20	0.18	0.39	8.16	69.3	0.020	12825
Beetroot leaf (unw)	1	109	0.63	60.5	13711	2.69	0.16	0.51	10.6	162	0.013	13480
Beetroot (w)	3	82.0	<0.5	28.6	2634	1.47	0.04	0.45	9.13	130	0.001	25073
Beetroot (unw)	3	511	<0.5	31.3	3048	1.59	0.19	2.49	10.92	599	0.001	31641
Broccoli (w)	3	71.8	<0.5	3.79	7098	0.19	0.04	0.57	5.24	111	0.001	30601
Broccoli (uw)	3	31.8	<0.5	2.66	6269	0.26	0.06	0.45	4.40	88	0.001	31510
Celery (w)	3	71.4	<0.5	18.7	4844	2.29	0.05	0.74	12.96	133	0.001	37544
Celery (uw)	3	5048	2.0	54.5	10073	5.25	1.87	12.0	14.93	4451	0.023	25120
Collard greens (w)	3	256	<0.5	29.8	17108	1.54	0.11	0.86	10.63	306	0.017	26049
Collard greens (uw)	3	410	<0.5	24.6	10911	1.21	0.30	1.44	8.64	648	0.009	18567
Daicon (w)	1	40.2	0.54	2.91	3984	1.15	0.13	0.39	4.29	63.7	0.002	16489
Daicon (uw)	1	195	0.71	3.72	3223	0.83	0.07	0.73	4.15	229	0.000	22922
Daicon leaf (w)	1	65.8	0.18	4.35	14931	1.96	0.05	0.42	5.54	92.8	0.007	14663
Daicon leaf (uw)	1	465	0.43	9.14	21687	3.02	0.22	1.19	5.44	503	0.013	15351
Leak (w)	1	21.0	0.10	3.95	2964	0.40	0.08	0.27	6.78	49.8	0.006	17206
Leak (uw)	1	53.2	<0.5	2.32	5835	0.54	0.13	0.40	6.43	85.8	0.009	19304
Onion	4	28.3	<0.5	1.31	1120	0.92	0.05	0.25	3.51	64.5	0.001	11031
Parsnip (w)	3	234	<0.5	27.8	4537	0.67	0.16	1.22	8.78	349	0.008	26166
Parsnip (uw)	3	580	<0.5	44.4	5540	0.94	0.12	1.92	14.3	642	0.010	23773
Paper	4	10.8	0.34	0.75	1986	1.68	0.02	0.31	5.52	53.7	0.001	20492
Paper leaf	4	67.4	0.63	6.35	25559	5.56	0.11	0.38	5.63	94.6	0.002	20327
Parsley (w)	1	129	0.31	40.9	15478	1.12	0.08	0.48	6.70	173	0.005	14385
Parsley (uw)	1	261	0.38	42.3	14338	1.41	0.10	0.90	7.63	262	0.002	19058
Parsley (w)	2	245	0.78	13.36	10896	0.22	0.10	0.99	33.7	326	0.004	33641
Parsley (uw)	2	502	0.68	14.7	10161	0.44	0.21	1.45	52.9	559	0.005	29935
Parsley	5	150	<0.5	17.0	17112	0.67	0.08	0.59	11.2	173	0.004	24859
Potato (w)	2	12.6	0.43	1.42	425	0.63	0.04	0.21	9.10	40.5	0.001	20733
Potato (uw)	2	24.4	0.37	0.73	394	0.67	0.03	0.32	10.5	67.0	0.001	20603
Potato	4	16.9	<0.5	1.56	662	0.56	0.06	0.23	5.04	44.6	0.001	21892
Potato leaf	4	397	0.67	10.1	7110	1.29	0.11	1.11	9.82	438	0.001	29198
Radish (w)	2	66.8	0.10	3.94	4423	1.06	0.23	0.58	7.20	107	0.001	29558
Radish (uw)	2	512	0.06	7.43	5139	1.18	0.43	1.69	8.97	658	0.001	29463
Radish leaf (w)	2	131	0.19	9.78	23550	2.74	0.19	0.51	20.7	168	0.002	6249
Radish leaf (uw)	2	1590	1.00	23.6	32763	3.79	0.97	3.28	64.1	1553	0.011	10347
Tomato	4	7.69	<0.5	0.72	2738	0.97	0.01	0.19	6.84	52.6	0.001	21886
White icecicle (w)	3	89.3	<0.5	6.22	6197	2.54	0.22	0.70	7.89	127	0.001	29828
White icecicle (uw)	3	580	<0.5	7.90	4625	1.28	0.46	2.08	8.83	757	0.001	34590
White icecicle leaf (w)	3	538	1.10	18.04	32918	4.31	0.34	1.43	104	528	0.013	13136
White icecicle leaf (uw)	3	794	<0.5	17.83	33484	2.49	0.55	2.15	185	918	0.012	12304
Average		347	0.55	16.09	9714	1.64	0.21	1.13	17.78	384	0.01	21914
Minimum		7.69	0.06	0.55	394	0.19	0.01	0.19	3.51	40.5	0.001	6249
Maximum		5048	2.0	60.5	33484	5.56	1.87	12	185	4451	0.02	37544
		Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe	Hg	K
MPL, dry			1.0			0.3					0.1	
MPL, fresh			0.3			0.05					0.02	



Table 2b: The content of the analyzed elements in vegetable samples taken from the 5 location (given in mg kg-1 dry mass)

Vegetable	Garden No.	Li	Mg	Mn	Mo	Na	Ni	P	Pb	Sr	V	Zn
Aubergine	4	0.09	3218	6.46	0.22	251	0.64	1958	5.23	0.8	0.06	21.2
Beetroot (w)	1	0.15	2971	6.50	<0.1	5447	0.30	2773	6.95	8.2	0.07	36.9
Beetroot (unw)	1	0.16	2416	8.08	<0.1	6470	0.33	2395	5.68	7.0	0.28	28.4
Beetroot leaf (w)	1	6.05	5721	27.26	0.30	22984	0.38	1649	3.71	38.3	0.02	59.1
Beetroot leaf (unw)	1	4.36	6217	28.02	0.15	18543	0.74	2218	4.10	36.0	0.20	57.5
Beetroot (w)	3	0.12	4753	12.6	0.05	9941	0.98	1604	5.14	14.2	0.28	37.0
Beetroot (unw)	3	0.34	4905	23.2	0.22	11286	1.31	1985	7.96	17.6	1.77	41.1
Broccoli (w)	3	0.07	4081	14.6	0.35	1628	0.84	5982	5.36	16.4	0.13	39.3
Broccoli (uw)	3	0.05	3731	15.1	0.30	1611	0.72	6385	5.37	13.9	0.03	37.8
Celery (w)	3	0.06	3732	17.5	0.08	2241	1.69	8063	6.04	31.6	0.22	35.4
Celery (uw)	3	2.96	4819	141	0.10	2724	9.21	3736	32.4	53.4	15.16	67.0
Collard greens (w)	3	1.16	5392	36.6	0.28	10332	0.83	2164	6.28	36.4	0.70	35.6
Collard greens (uw)	3	0.61	5002	69.7	0.10	13196	1.47	1971	7.14	29.1	1.27	28.6
Daicon (w)	1	0.07	3134	11.7	0.32	8656	2.33	2558	3.70	17.9	0.07	27.3
Daicon (uw)	1	0.16	2595	12.8	0.29	8699	2.04	2730	5.08	15.9	0.47	26.0
Daicon leaf (w)	1	0.25	3510	42.9	0.14	9883	1.37	2150	3.67	39.6	0.10	22.0
Daicon leaf (uw)	1	0.66	3974	70.0	0.40	13209	2.56	2244	5.59	54.9	1.21	29.3
Leak (w)	1	0.05	2932	5.80	0.13	972	0.46	1413	5.88	15.5	0.02	19.1
Leak (uw)	1	0.12	3020	13.8	0.13	1216	0.62	2112	4.57	10.6	0.08	20.4
Onion	4	0.03	2531	9.57	0.10	585	1.01	2180	5.35	3.5	0.06	21.2
Parsnip (w)	3	0.19	5084	21.2	0.19	426	1.58	2763	7.59	24.2	0.75	20.3
Parsnip (uw)	3	0.36	4806	25.5	0.11	694	1.89	3575	9.63	29.4	1.66	33.8
Paper	4	0.14	3344	6.93	0.10	188	0.79	2486	5.21	3.8	0.02	19.7
Paper leaf	4	1.62	5640	29.4	0.10	55	0.73	1618	4.74	51.0	0.13	39.9
Parsley (w)	1	0.20	4610	34.8	1.35	6519	1.13	1741	5.39	40.6	0.29	47.8
Parsley (uw)	1	0.24	5526	37.2	1.36	6763	1.56	2234	6.18	39.6	0.61	49.1
Parsley (w)	2	0.26	4358	34.7	0.70	2826	1.79	1542	6.91	20.5	0.71	27.1
Parsley (uw)	2	0.39	4283	41.1	0.45	3274	2.04	1454	7.82	19.3	1.38	29.3
Parsley	5	4.83	5294	67.4	1.63	6416	1.68	3075	5.61	57.8	0.31	63.9
Potato (w)	2	0.01	2685	4.69	0.10	80	0.44	2378	5.44	1.3	0.07	20.8
Potato (uw)	2	0.04	2989	5.75	0.16	94	0.51	2546	5.75	1.2	0.07	22.2
Potato	4	0.03	2168	4.01	0.10	84	1.04	1828	5.87	2.0	0.09	18.6
Potato leaf	4	0.30	5507	26.7	0.53	40	1.45	2690	6.92	13.5	1.06	25.7
Radish (w)	2	0.08	3486	12.9	0.28	7086	0.63	2853	4.85	13.9	0.19	30.2
Radish (uw)	2	0.35	3817	25.8	0.24	6403	1.68	2683	7.52	17.7	1.68	36.2
Radish leaf (w)	2	0.26	4780	42.7	0.40	5201	1.09	1080	6.68	48.9	0.33	38.8
Radish leaf (uw)	2	1.05	5183	102	0.40	6181	3.60	1780	12.7	73.7	4.39	62.2
Tomato	4	0.06	3466	8.86	0.48	1401	0.31	2572	5.05	7.6	0.04	19.2
White icecicle (w)	3	0.07	4062	13.4	0.16	10704	2.92	4125	5.26	19.7	0.19	39.9
White icecicle (uw)	3	0.41	3785	24.6	0.10	9205	2.94	4189	9.16	17.0	1.74	43.3
White icecicle leaf (w)	3	0.48	4825	52.4	0.38	13162	2.07	3073	9.92	68.7	1.43	32.9
White icecicle leaf (uw)	3	0.78	5482	60.1	0.24	11534	2.20	2565	9.11	67.9	2.12	32.2
Average		0.71	4139	29.89	0.33	5910	1.52	2693	6.87	26.19	0.99	34.36
Minimum		0.01	2168	4.01	0.05	40	0.3	1080	3.67	0.8	0.02	18.6
Maximum		6.05	6217	141	1.63	22984	9.21	8063	32.4	73.7	15.2	67.0
MPL, dry									3.0			
MPL, fresh									0.1			

MPL – Maximal Permitted Level; w- washed samples; uw – unwashed samples



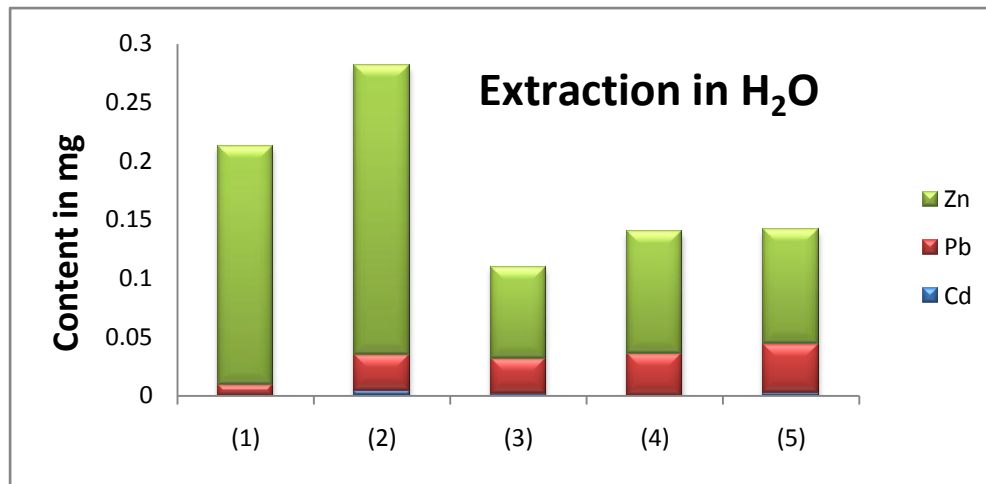


Figure 3: Extraction for Cd, Pb and Zn in H₂O extraction solution of soil from gardens where the vegetable species were taken

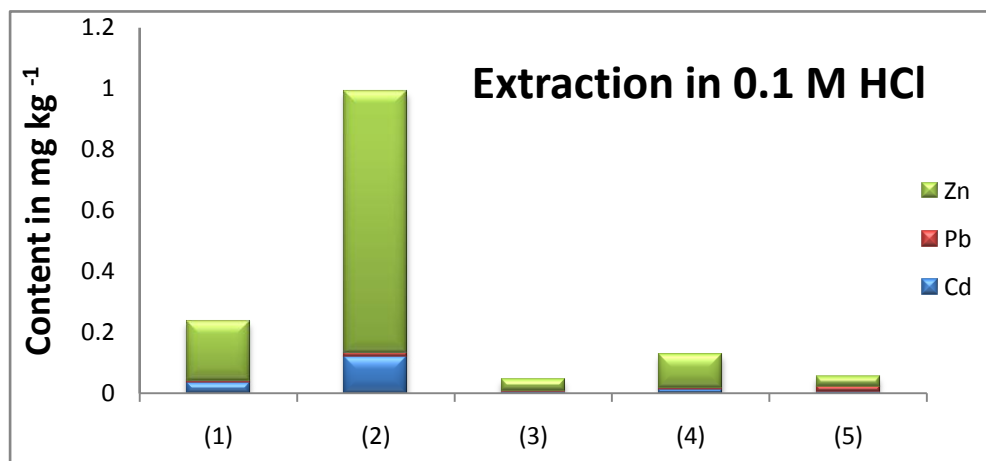


Figure 4: Extraction for Cd, Pb and Zn in HCl extraction solution of soil from gardens where the vegetable species were taken

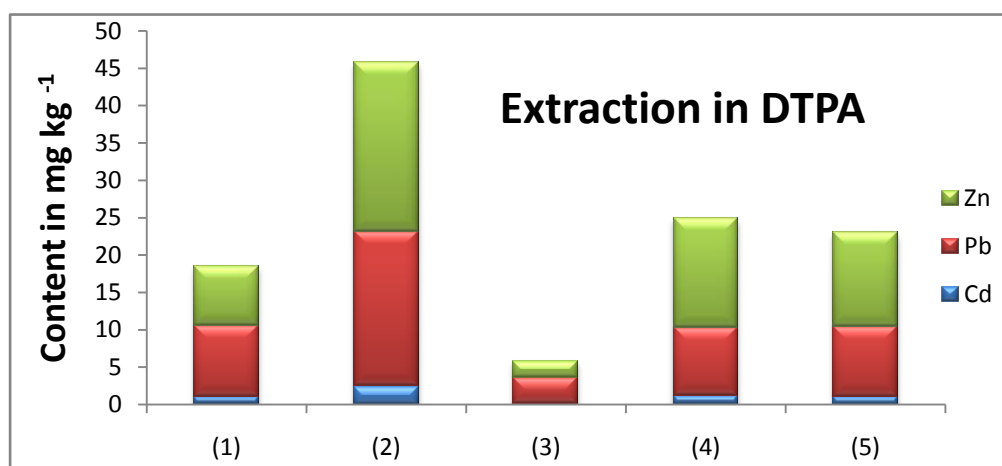


Figure 5: Extraction for Cd, Pb and Zn in (DTPA-TEA-CaCl₂x2H₂O) extraction solution of soil from gardens where the vegetable species were taken

Content of extractible Cd in 0.1 mol L⁻¹ HCl (Fig. 4) for soil from the gardens No. 1, 3, 4 and 5 is in the range of 0.0036 to 0.0359 mg kg⁻¹, but the content of extractible Cd in garden No. 2 is higher (0.12 mg kg⁻¹). The content of extractible zinc in 0.1 mol L⁻¹ HCl (Fig. 4) for soils from the locations No. 1 and 2 is very higher (0.192 mg kg⁻¹ and 0.857 mg kg⁻¹, respectively) but the content of extractible Zn for the other gardens soil is low and ranges from 0.031 to 0.108 mg kg⁻¹. The content of extractible Pb in 0.1 mol L⁻¹ HCl (Fig. 4) for locations No. 1, 3 and 4 is in the range of 0.006 to 0.007 mg kg⁻¹, but for locations no. 2 and 5 is in the range of 0.014 to 0.019 mg kg⁻¹ and it is higher than content on location no. 1, 3 and 4.

With solution of DTPA we simulate the process that is unrolling in the nature condition between the garden soil and roots. The content of zinc and lead is similar but for cadmium is the less (Fig. 5). Extraction with DTPA (DTPA-CaCl₂-TEA) from the soil samples in all gardens, present a real condition in nature for the process of accumulation on metals by the vegetable. Content of extractible zinc is in the range of 2.22 to 22.6 mg kg⁻¹, for extractible lead is in the range of 3.50 to 20.7 mg kg⁻¹ and content of extractible cadmium is in the range of 0.07 to 1.21 mg kg⁻¹. Extraction order for cadmium, lead and zinc from the analyzed gardens soil with DTPA solution as follows: Cd > Pb > Zn, for Cd < 27%, for Pb < 10% and for Zn < 7.9%. This is the reason for the high content of Cd and Pb (over the permitted levels) in most of the analyzed vegetables.

Assimilation by vegetables

Bioaccumulation of Cd, Pb and Zn as toxic elements may have a serious affect to the human health. For that reason, we made this examination of distribution and accumulation for Cd, Pb and Zn and more other elements in edible parts of 7 species of vegetables which is grown up in the area around the smelter for lead and zinc. Using the results of the analysis of Cd, Pb and Zn and more other elements in different plant parts (root, stems and leaves), we may to present, the *Biological Accumulation Factor* (BAF), defined as the ratio between total content in certain plant (sum of the content in root, stems or leaves) to the content of the element in corresponding soil. Data for Biological Accumulation Factor are present in Table 3 and the highest factor was obtained for Cd, and then for Zn and Pb (Cd > Zn > Pb).

Table 3: Bioaccumulation factor for various vegetables (in mg kg⁻¹)

Sample	Root	Steam/Leaf	Sum	Soil	BAF ¹
Garden No. 1					
Cd					
Leak	0.40	0.54	0.94	6.77	0.13
Beetroot	0.62	3.20	3.82	6.77	0.56
Daicon	1.15	1.96	3.11	6.77	0.46
Pb					
Leak	5.88	4.57	10.4	156	0.067
Beetroot	6.95	3.71	10.7	156	0.068
Daicon	3.70	3.67	7.37	156	0.047
Zn					
Leak	19.1	20.4	39.5	231	0.17
Beetroot	36.9	59.1	96.0	231	0.42
Daicon	27.3	22.0	49.3	231	0.21
Garden No. 2					
Cd					
Radish	1.06	2.74	3.80	8.72	0.44
Pb					
Radish	4.85	6.68	11.5	189	0.061
Zn					
Radish	30.2	38.8	69.0	284	0.24
Garden No. 3					
Cd					
White icecele	2.54	4.31	6.85	1.39	4.93
Pb					
White icecele	5.26	9.92	15.2	46.0	0.33
Zn					
White icecele	39.9	32.9	72.8	65.3	1.11
Garden No. 4					
Cd					



Potato	0.56	1.29	1.85	7.66	0.24
Green pepper	1.68	5.56	7.24	7.66	0.94
Pb					
Potato	5.87	6.92	12.8	138	0.09
Green pepper	5.21	4.74	9.95	138	0.07
Zn					
Potato	18.6	25.7	44.3	228.8	0.19
Green pepper	19.7	39.9	59.6	228.8	0.26

BAF – Bioaccumulation factor (Biological Accumulation Factor): the ratio between the total content of the element in the root + stem/leaf and that present in the soil.

Conclusion

The intensive uncontrolled processing of pollution from Pb-Zn plant in the past has resulted with large amounts of heavy metals in soils from the town of Veles and its environs. This is the reason for high content of heavy metals to be present in the surrounding soils. It was found that the content of Cd in soils from 5 vegetable gardens situated near the town was 10 times over the referent value according to the new Dutch list for Cd while the content of Pb and Zn was 2 times over the appropriate referent values for these elements. Vegetables grown in the nearby sites were also contaminated by the relevant heavy metals, especially Cd and Pb, which could be a potential health concern to local residents. It was found that the content of Cd, Pb and Zn in vegetables exceeded the maximum permissible concentration. The content of Cd ranges from 0.55 mg kg⁻¹ in beetroot to 5.56 mg kg⁻¹ in green pepper-leaf. Average value for Cd for all 42 vegetable samples (washed and unwashed) is 1.64 mg kg⁻¹. All these three values are over the maximal permitted limit (MPL) of 0.3 mg kg⁻¹ for Cd in dry vegetable. The content of Pb ranges from 3.67 mg kg⁻¹ in daicon-leaf to the maximal value of 32.4 mg kg⁻¹ in celery with average value for Pb of 6.87 mg kg⁻¹ exceeding the MPL (3.0 mg kg⁻¹) in all vegetable samples. Also, the presence of zinc is in high ranges from 18.6 to 67.0 mg kg⁻¹, with 34.36 mg kg⁻¹ average value. Extraction order for cadmium, lead and zinc from the analyzed gardens with DTPA solution as follows: Cd >Pb>Zn, for Cd<27%, for Pb<10% and for Zn<7.9%. Thus, the content of Cd and Pb is several times higher in all 14 sorts of analyzed vegetables than the permitted level.

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