Heavy Metals and Metalloid Content in Vegetables and Soil Collected from the Gardens of Zagreb, Croatia

Puntarić, Dinko; Vidosavljević, Domagoj; Gvozdić, Vlatka; Puntarić, Eda; Puntarić, Ida; Mayer, Dijana; Bošnir, Jasna; Lasić, Dario; Jergović, Matijana; Klarić, Ivana; ...

Source / Izvornik: Collegium antropologicum, 2013, 37, 957 - 964

Journal article, Published version Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

Permanent link / Trajna poveznica: https://urn.nsk.hr/um:nbn:hr:151:315633

Rights / Prava: In copyright/Zaštićeno autorskim pravom.

Download date / Datum preuzimanja: 2024-11-23



Sveučilište Josipa Jurja Strossmayera u Osijeku **Fakultet**

agrobiotehničkih znanosti Osijek Repository / Repozitorij:

Repository of the Faculty of Agrobiotechnical Sciences Osijek - Repository of the Faculty of Agrobiotechnical Sciences Osijek





Heavy Metals and Metalloid Content in Vegetables and Soil Collected from the Gardens of Zagreb, Croatia

Dinko Puntarić¹, Domagoj Vidosavljević^{1,2}, Vlatka Gvozdić³, Eda Puntarić⁴, Ida Puntarić⁵, Dijana Mayer⁶, Jasna Bošnir⁷, Dario Lasić⁷, Matijana Jergović⁷, Ivana Klarić⁸, Marina Vidosavljević⁹ and Ivančica Krivdić¹⁰

¹ »Josip Juraj Strossmayer« University Osijek, School of Medicine, Department of Public Health, Osijek, Croatia

- ² Vukovar General Hospital, Vukovar, Croatia
- ³ »Josip Juraj Strossmayer« University Osijek, Department of Chemistry, Osijek, Croatia
- 4 University of Zagreb, Faculty of Science, Biology Department, Environmental Sciences Direction, Zagreb, Croatia
- ⁵ Zagreb County Institute for Emergency Medicine, Velika Gorica, Croatia
- ⁶ Croatian National Institute of Public Health, Zagreb, Croatia
- ⁷ Zagreb Public Health Institute, Department of Health Ecology, Zagreb, Croatia
- ⁸ »Josip Juraj Strossmayer« University Osijek, Faculty of Agriculture, Osijek, Croatia
- ⁹ Vinkovci General Hospital, Department for Internal Medicine, Vinkovci, Croatia

¹⁰ SINACO Ltd., Zagreb, Croatia

ABSTRACT

Aim of this study was to determine concentration of Pb, Cd, As and Hg in green leafy vegetables and soil in the urban area of Zagreb, Croatia and to determine if there is a connection between the contamination of soil and vegetables. Green leafy vegetables and soil samples were taken from the gardens located in the outskirts of the city. Concentrations of Pb, Cd, As and Hg were determined by atomic absorption spectrometry; showing that average concentrations of metals and metalloids in vegetables and in soil, regardless of the location of samplingwere below the maximum allowed concentration (MAC). The analysis determined thatmetal concentrations in only nine vegetable samples (9%) were above maximum allowed values prescribed by national and European legislation (three with higher concentrations of Pb, one with a higher concentration of Cd and five with higher concentrations of Hg). Concentrations of contaminants present in the analysed samples, in general, are lower than the ones published in similar studies. The final distribution and concentration of contaminants in vegetables of Zagreb, besides industry and traffic, is affected by the dominant wind direction.

Key words: atomic absorption spectroscopy, metals, metalloids, soil, vegetables, Zagreb

Introduction

Interest in studying heavy metals in ecosystems is focused on soil, plants, animals and ultimately, via the food chain, in humans. The main route of contamination by heavy metals is through the disposal of substances from the atmosphere, for which the main source is industrial activity^{1–3}. Other important ways of contamination of agricultural land include a variety of urban activities: use of herbicides, pesticides, fertilizers and by industrial and municipal wastewater^{4–6} The tradition of growing vegetables in the outskirts of the city is widespread because such production has a distinct commercial advantage (growing vegetables near the market where they are sold) or it is intended for the grower's personal use.

Unfortunately, peri-urban agriculture is practiced in many unsuitable areas, such are the free fallow land near the factories, major roads or areas around residential buildings in the vicinity of landfill sites⁷. Metals in the

Received for publication May 9, 2010

environment represent a special problem because of their long lasting and direct effect on human health. Their toxicity can be observed through the impairment of enzyme function by replacing the essential elements, removing the essential elements from the pigments and producing reactive oxygen species⁸.

Among all the metals, lead (Pb), cadmium (Cd), mercury (Hg) and arsenic (As) have been recognized as a major problem because of their unquestionable toxicity, non-biodegradability and accumulation in vital organs of animals and humans, causing various clinical conditions even in smaller concentrations^{9,10}.

The population intake of heavy metals through the food chain represents a significant public health problem in many countries, especially underdeveloped countries, and requires more attention^{11,12}.

Leafy vegetables are of particular interest for biomonitoring of heavy metals and metalloids deposition in the environment.

Due to a higher degree of translocation and transpiration in relation to other vegetables, leafy vegetables are used as a bioindicator for lead, cadmium, iron, arsenic and $zinc^{13}$.

Spinach (Spinacea oleracea), lettuce (Lettuce sauce sativa) and endive (Cichorium endivia) have been used successfully for bioaccumulation control in heavy metals precipitation in the gardens of industrial and residential areas¹⁴.

The Republic of Croatia before the war for independence (1991 – 1995) was a country with highly developed metal, chemical and food industries, mainly of »socialist type«, with little concern for the environment. After the war, de-industrialization has been recorded, but the industries based on »dirty technology« have survived and continue to function on the same principles as before.

Zagreb is the capital of Croatia, a small country in transition located in central Europe. According to the 2001 census it accounts for 779.145 or 17.6% of the total Croatian population, with a surface area of 641.36 km².

Research of pollution in Zagreb over the years of continuous measurements and individual studies of soil¹⁵ and air¹⁶ have shown an increased presence of metals and metalloids. There are limited studies of heavy metals contamination on plants in and around of Zagreb.

Research results of Pb concentrations in the leaves of the yew tree (*Taxus baccata L.*) show that the contamination of plants depends on the distance from major roads and traffic intensity in general¹⁵. Research of Pb concentrations in Brassicas grown in home gardens in the city of Zagreb has showed that the highest concentration of Pb in vegetables was found in the southern and southwestern parts of the city under the influence of traffic and the prevailing winds⁴.

Zagreb has an additional problem with waste disposal. Some attempts to solve the problem ended in failure, creating additional environmental problems. The most infamous case was a fire in the waste incineration facility »Puto« (the only waste incinerator in Croatia), only 5 km away from the city centre. In August 2002 improperly stored waste of unknown composition that was prepared for incineration caught fire. As a consequence, more than 250 tons of ash and other waste were left on the site^{16,18}. This disaster was one of the main reasons for this research.

The aim of the study was to assess possible sources and the level of contamination in leafy vegetables and soil with Pb, Cd, As and Hg; population exposure to these metals in vegetables, soil and air in Zagreb and to compare newly obtained results with previous research⁴.

Materials and Methods

Study area

City of Zagreb is located in northern Croatia, on the banks of the Sava River, 170 km from the Adriatic Sea, at 45° 10; 15' north latitude and 15° 30' east longitude. It is situated at 122 meters above sea level. The climate is continental with an average summer temperature of +20 °C and an average winter temperature of +1 °C¹⁹.

Sampling of soil and vegetables

Vegetable and soil sampling was carried according to compass - in the east, south, west and north of the Zagreb city centre.

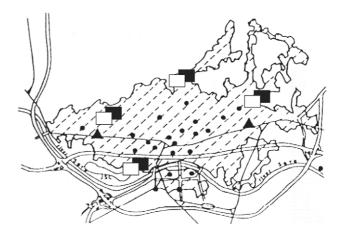


Fig. 1. A map of the city of Zagreb with the sampling sites for vegetables and soil (Hg, Cd, As and Pb concentration measurement). Circles: the sites of metal and metalloids in atmospheric precipitations. Triangles: the sites of metal processing plants. Rectangles: the sites of Pb, Cd, As and Hg measurement in green leafy vegetables (black rectangles) and soil (white rectangles)

The research included the location of private gardens in the city of Zagreb. One hundred (100) samples of leafy vegetables (25 on each side of the world) and 16 samples of soil from the same location (four at each site) were collected. Among thesamples ofleafy vegetables were the most common, lettuce (*Lactuca sativa*) with 22 samples, collards (Kale) (*Brassica oleracea var. Capitata f. savoy*) with 19 samples, chard (Swiss chard) (*Beta vulgaris var.* Cicla) with 17 samples, cabbage (white cabbage) (Brassica oleracea var. capitata f. alba) with 11 samples and spinach (Spinacea oleracea) with nine samples. The other species that were sampled included: leek (Allium ampeloprasum ssp. Porrum), parsley leaves (Petroselinum crispum), rhubarb (Rheum rabarbarum), red beet leaves (beet-Beta vulgaris var. Conditiva), dill(Anethum graveolens var. hortorum), broccoli (Brassica oleracea var. italica), radishes(Raphanus sativus var. sativus), collards (red cabbage) (Brassica oleracea var. acephala), horseradish leaves (Armoracia rusticana) and celery (celeriac-Apium graveolens var. secalinum).

Plant and soil analysis

Vegetable samples were washed under running water for 5 minutes, cut and homogenized. A two gram of homogenized sample was added to 5 mL 65% HNO3 and 1.0 mL 40% H_2O_2 and digested in a microwave oven. Preparation of the soil samples was done according to the ISO 11466:2004 method. Soil samples were dissolved in Aqua Regia and in the same way as the vegetable samples were digested in a microwave oven (Anton Paar, MULTIWAVE 300, Perkin Elmer-Anton Paar, Italy). Metal and metalloid concentrations were determined by atomic absorption spectrometry (AAS); the graphite furnace technique was used for Pb and Cd, the hydride generation technique for As (Perkin Elmer PE 4110 ZL, Shelton, USA), and the cold vapour technique for Hg (FIMS 400, Shelton, USA). Limits of quantification (LOQ) for each metal/metalloid were 2.0 μ g/L for Pb, 0.2 μ g/L or Cd, 0.5 μ g/L for As and 0.1 μ g/L for Hg²⁰.

LOQ were based on the following criteria: standard deviations for consecutive metal/metalloids measurements in the blank sample were multiplied by 10, with a subsequent addition of the metal/metalloid concentration measured in the blank sample. Calibration curves were created using Pb, Cd, As and Hg stock standard solutions (1000 mg/L. Merck, Germany) adequately diluted with Milli-Q water, prepared on the day of analysis. To assure the quality of metal determination, all measurements were performed in triplicate. Measured metal/ metalloid concentrations in the digestion solutions were expressed as $\mu g/mL$. The final results ($\mu g/L$) were obtained by multiplying the measured metal/metalloid) concentration $(\mu g/mL)$ with the dilution volume (mL), and dividing it with sample weights (g). Analytical quality was assured through the regular participation of the laboratory in proficiency testing studies (PTS) organized by the Food and Environment Research Agency, UK and Interuniversity Department for Agrarbiotechnologie, IFA-Tulin, Austria.

Wind data for this study was obtained from the State Hydrometeorology Institute Zagreb.

The Statistica software, version 8.0 (StatSoft, Inc., 2008) was used for data analysis and the Pearson correlation analysis was performed. The level of significance was set at P < 0.05.

Results

The results of the analysis of Pb, Cd, As and Hg in the leafy parts of vegetables and in the soil are shown in Tables 1–3.

Mean concentrations of Pb, Cd, As and Hg in leafy vegetables from Zagreb were within the maximum allowed concentration (MAC) for green leafy vegetables²¹.

However, nine (9%) samples recorded values above the MAC: Pb was higher in three samples; Cd in one, Hg was higher in five samples. Arsenic was not found increased in any of the samples.

According to the sampling locations, two samples with increased Pb and one with higher Hg were recorded in vegetables grown in eastern parts of the city. One sample with increased Pb and Cd was recorded in the western part of the city. In the samples taken in the northern part of the city a total of four vegetable samples with higher values of Hg were found. In the vegetable samples taken from the southern part of the city (location of the waste incineration facility »Puto«) there were no samples with increased values of the metals and metalloids in question (Table 1).

Mean concentrations of Pb, Cd, As and Hg in the soil of Zagreb regardless of the sampling locations, were within the MAC, both by the usual criteria of the highest allowable amounts of contaminants in agricultural soils and the stricter criteria of limit values of harmful substances in the soil that can be used for organic production²².

However, in samples taken from the western part of the city, five (31.3%) soil samples recorded Pb values that were above the MAC by both criteria, while in two (12,5%) samples increased levels of Pb according to the criteria for agricultural land were found.

According to the criteria for organic production, an additional three samples with higher As in the northern part of the city were found (Table 2).

Looking at samples of vegetables and soil together, it can be observed that only in the samples of vegetables and soil taken from the western part of the city, increased values of Pb were found (one vegetable and two soil samples with Pb).

Similarly, in the north, we have found four samples of vegetables with high Hg and three soil samples with high As (according to the criteria of soil for organic production).

In the samples collected from the southern part of the city there were no vegetable or soil samples with higher values, while in the east contamination was found only in vegetables (Table 3).

Although measured values were not high, the Pearson correlation analysis revealed a significant correlation (p < 0.05) between Hg in soil and vegetables in the eastern part (0.97), and between Cd in soil and vegetables (0.93) in the samples taken from the western part of the city.

Meteorological data collected for the period from early 1995 until the end of 2006 showed the prevalence of

 TABLE 1

 PB, CD, AS AND HG CONCENTRATION IN GREEN LEAFY VEGETABLE SAMPLES FROM THE CITY OF ZAGREB WITH REGARD TO MAC – MAXIMUM ALLOWED CONCENTRATIONAND SAMPLING LOCATIONS

City area	No Aritmetic n		Standard deviation	Range	Median	
		Pb (M	AC=0.30 mg/kg)*			
East	25	0.14	0.09	0.05 - 0.42	0.13	
South	25	0.06	0.03	0.05 - 0.15	0.05	
West	25	0.11	0.08	0.05 - 0.38	0.08	
North	25	0.10	0.06	0.05 - 0.22	0.06	
Total	100	0.10	0.07	0.05 - 0.42	0.08	
		Cd (M	AC=0.20 mg/kg)*			
East 25 0.02 South 25 0.02	0.02	0.01	0.01 - 0.03	0.02		
	0.02	0.02	0.01 - 0.04	0.02		
West			0.08	0.01 - 0.41	0.02	
North			0.01	0.01 - 0.05	0.01	
Total 100		0.02	0.04	0.01 - 0.05	0.01	
		As (M	AC=0.30 mg/kg)*			
East	25	0.02	0.01	0.02 - 0.08	0.02	
South 25 0		0.02	0.02 0.00		0.02	
Vest 25	0.02	0.00	0.02 - 0.02	0.02		
North 25		0.02	0.00	00 0.02–0.03		
Total	100	0.02	0.01	0.02-0.08	0.02	
		Hg (M	AC=0.050 mg/kg)*			
East 25 0.		0.011	0.014	0.003 - 0.056	0.006	
South	25 0.003		0.000	0.002 - 0.007	0.002	
West	25	0.002	0.001	0.002 - 0.007	0.001	
North	25	0.020	0.039	0.002 - 0.130	0.039	
Total	100	0.009	0.022	0.002-0.130	0.030	

* According to: Republic of Croatia. Act on toxins, metal, metalloids and other harmful substances present in food. Official Gazette of the Republic of Croatia (Narodne novine) 2005:16. (in Croatian)

winds of the northern, north-eastern, south-eastern and north-western directions (Figure 2).

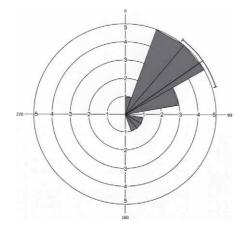


Fig. 2. Prevailing wind of the city of Zagreb during the period from January 1995 to December 2006, according to the data by the national Weather service, showing the predominance of the north, northeast, southeast and northwest direction.

Discussion

Vegetables that are grown within urban or suburban areas are good indicators of environmental pollution^{13,14,17}. Some of them like lettuce, chard and spinach, which in our study represented 48% of samples, have a particularly high degree of relative accumulation of metals. Besides them, cabbage, red cabbage, radishes and beets, which have an intermediate to high level metals accumulation, represented a further 15% of vegetables samples in our study²³.

Soil samples were collected from the gardens and estimated by the usual criteria for agricultural lands, and the stricter criteria for organic production^{21,22}.

All mean concentrations of elements studied in soil samples were within the allowed values, regardless of the location of sampling. Among soils from the gardens two (12.5%) of them were found with high values of Hg according to the criteria for agricultural soil, and an additional three (18.8%) samples had high values of As according to the criteria for organic production.

TABLE 2	
PB, CD, AS AND HG CONCENTRATION IN SOIL SAMPLES FROM THE CITY OF ZAGREB WITH REGARD TO MAC	С
– MAXIMUM ALLOWED CONCENTRATIONAND SAMPLING LOCATIONS	

City area No		Aritmetic mean Standard deviation		Range	Median	
		Pb (MAC=50 m	g/kg)*(MAC=100 mg/kg)**	¢.		
East	4	6.67	AC=50 mg/kg)*(MAC=100 mg/kg)** 37 9.53 39 17.11 59 74.60 37 14.09 46 43.46 AC=0.80 mg/kg)*(MAC=1.0 mg/kg)** 8 0.10 3 0.17 5 0.21 2 0.16 3 0.17 5 0.21 2 0.16 3 0.17 2=10.00 mg/kg)*(MAC=20.00 mg/kg)** 15 1.23 78 2.44 19 1.71	3.84 - 26.90	14.90	
South	4	14.69	17.11	3.84-26.90 2.27-34.70 0.25-150.00 3.84-32.40 0.25-150.00 0.12-0.50 0.17-0.66 0.14-0.48 0.02-0.66 * 6.11-8.74 0.50-5.85 4.17-8.34 5.59-17.40 0.50-17.40 0.05-0.10 0.07-0.11 0.07-0.47	15.94	
West	4	63.59	74.60	0.25 - 150.00	71.70	
North	4	11.67		13.25		
Total	16	27.46	43.46	0.25 - 150.00	18.05	
		Cd (MAC=0.80 r	mg/kg)*(MAC=1.0 mg/kg)*	*		
East 4 South 4 West 4	0.08	0.10	0.02 - 0.24	0.14		
South 4 0.13		0.13	0.17	0.12 - 0.50	0.24	
West	4	0.15		0.17 - 0.66	0.29 0.17	
North	4	0.12		0.14-0.48		
Total	16	0.13	0.17	0.02-0.66	0.19	
		As (MAC=10.00 m	ng/kg)*(MAC=20.00 mg/kg)**		
East	4	7.15	1.23	6.11 - 8.74	6.87	
South	4	1.78	2.44	0.50 - 5.85	4.93	
West	4	6.19	0.17 0.21 0.16 0.17 .00 mg/kg)*(MAC=20.00 mg/kg)** 1.23 2.44 1.71 4.91 3.86 C=0.80 mg/kg)*(1.00 mg/kg)** 0.02	4.17-8.34	6.13	
North	4	11.57	4.91	5.59 - 17.40	11.65	
Total	16	12.69	3.86	0.50 - 17.40	6.18	
		Hg (MAC=0.8	80 mg/kg)*(1.00 mg/kg)**			
East	4	0.07	0.02	0.05 - 0.10	0.07	
South	4	0.10	0.02	0.07 - 0.11	0.11	
West	4	0.30	0.18	0.07 - 0.47	0.36	
North	4	0.16	0.04	0.11-0.20	0.16	
Total	16	0.09	0.13	0.05 - 0.47	0.11	

* According to: Republic of Croatia. Act on ecologic production of vegetables and plants, Official Gazette of the Republic of Croatia (Narodne novine) 2001:91. (in Croatian); ** According to: Republic of Croatia. Act on farmland protection from contamination with noxious substances. Official Gazette of the Republic of Croatia (Narodne novine) 1992:15. (in Croatian)

The urban periphery is not suitable locations for the so-called »organic« production of agricultural crops, so only two cases of soil with increased lead values are to be discussed. Comparing the results with the new state regulations, also in line with EU legislation, under which the permitted concentration of lead and 150 mg/kg for this type of soil, and that because of its prevalence in nature there are no criteria for arsenic, we can state that all soil samples in our study were within the allowed values²⁴.

Although there is an indisputable relationship between metals and metalloids from soil with those found in plants, it is dependent on a number of factors such as soil pH, the presence of microorganisms, the active metabolism of the plant, type and preferences etc.

In this context, there is an ambiguous relationship to each other, and sometimes it is actually difficult to even find a link between them^{4,15}.

We found elevated concentrations of Pb in vegetables and soil in only one region (west), but the Pearson correlation analysis showed only a nonsignificant negative correlation. This suggests that plants, especially green leafy vegetables, receive Pb largely through the leavesand that transmission through the roots requires long-term contamination of soil, higher levels of contamination and deeper penetration of Pb in the soil^{1,17}.

However, a significant correlation between Cd in soil and vegetables in the western part of Zagreb suggests a longer presence of Cd contamination in the soil and partial transfer in the plant, which is not surprising as it is known as the industrial area of town, with a significant road and railway intersection (European traffic corridor 10).

While the significant correlation of Hg in soil and vegetables in the eastern part of the city (thermal-heating plant and a battery factory) may suggest a longer presence of Hg contamination and transfer in the plant, generally high levels of Hg in vegetables in the north of the city (four samples, area without traffic or industry) apparently have some other origin.

TABLE 3							
NUMBER OF GREEN LEAFY VEGETABLE AND SOIL SAMPLES FROM THE CITY OF ZAGREB ABOVE MAC							
– MAXIMUM ALLOWED CONCENTRATION							

City area	Green leaf vegetables $(\%)^*$			Soil (%)**,***				Total	
	Pb	Cd	As	Hg	Pb	Cd	As	Hg	(%)
East	2 (8%)	-	-	1 (4%)	_	_	_	-	3 (12%)
South	-	_	-	_	_	-	_	-	_
West	1 (4%)	1 (4%)	-	_	2 (50%)	-	_	-	4 (26%)
North	-	-	-	4 (16%)	_	-	3~(75%)	-	7 (45.5%)
TOTAL	3 (3%)	1 (1%)	_	5(5%)	2 (12.5%)	-	3 (18.6%)	-	14 (12.1%)
City area	Green leaf vegetables $(\%)^*$				Soil (%)**,***				Total
	Pb	Cd	As	Hg	Pb	Cd	As	Hg	(%)
East	2 (8%)	-	-	1 (4%)	_	_	_	-	3 (12%)
South	-	_	-	-	_	-	_	-	_
West	1 (4%)	1 (4%)	-	-	2(50%)	-	_	-	4 (26%)
North	-	-	-	4 (16%)	_	_	3 (75%)	-	7 (45.5%)
TOTAL	3 (3%)	1 (1%)	_	5 (5%)	2(12.5%)	_	3 (18.6%)	_	14 (12.1%)

* According to: Republic of Croatia. Act on toxins, metal, metalloids and other harmful substances present in food. Official Gazette of the Republic of Croatia (Narodne novine) 2005:16. (in Croatian).

** According to: Republic of Croatia. Act on ecologic production of vegetables and plants, Official Gazette of the Republic of Croatia (Narodne novine) 2001:91. (in Croatian).

*** According to: Republic of Croatia. Act on farmland protection from contamination with noxious substances. Official Gazette of the Republic of Croatia (Narodne novine) 1992:15. (in Croatian)

Although Hg levels currently do not represent a significant health threat, it would certainly be important to conduct further studies with larger numbers of samples and continuous monitoring for a longer period of time.

Some references indicate that a possible explanation for higher Hg concentrations in this residential part of the city could be the fact that the city crematorium is located in the vicinity. Crematoria have shown to be a significant source of mercury in the environment, due to mercury coming from dental amalgam fillings of the deceased. Some reports even predict that future growth of Hg from this source in the next twenty years could be expected²⁵.

Comparing our research with similar studies conducted during 1995 and 2002, we can generally say that the results are better (as in the number samples, as well as concentrations of contaminants present in the samples) and that vegetables grown in urban areas are (with exceptions) safe for human consumption.

The eastern part of the city is the industrial zone, dominated by a thermal-heating plant and a battery factory. The southern part of the town is dominated by the waste incinerator »Puto« that was destroyed in a fire and the European traffic corridor. The western part of the city is an industrial zone with very dense roads and rail transport (part of the European railway and traffic corridor 10), while the northern part of the city's urban areas, located on the slopes of Medvednica Mountain is almost an exclusive residential part of the city is intended only for housing and protected from industry and traffic.

It is difficult, therefore, without additional analysis, to understand how it is possible that in the south, certainly the busiest part of town, the area close to the incinerator and the waste depot, we did not find any sample of any vegetable or soil with high values of metals and metalloids, whereas in the north, an area free from traffic and industry, we found the largest number of samples and vegetables (four) and soil (three) with samples above the allowed concentrations. Part of the answer seems to be in the meteorological conditions. According to the Central Meteorological Bureau Station Maksimir of the State Hydrometeorology Institute for the period between 1995 and 2006, wind prevailed in the northern (1672 cases), north (1263 cases), southeast (862 cases) and north (851cases) direction (Figure 2). This means that the dominant winds raise contaminants from the eastern part and »leave« them in the northern part of the city. Moving by air through the city centre, oppressed by traffic and dense housing, contaminants are being transported by the wind to the west of the city where they merge with contaminants from traffic and industrial sources. That has resulted in the highest values of Pb in the soil and the highest concentrations of Cd and Pb in vegetables measured in the western part of the city.

Comparing these results with other published works, there is consistency in the findings according to the level of economic development and »environmental awareness«. Measured concentrations of Pb and Cd in vegetables grown in Zagreb were lower than those found in Sydney in 2004²⁶ with lower Pb concentrations in the soil of Zagreb than those measured in Sweden in 2003²⁷.

Measured concentrations of As in vegetables in Zagreb are approximately the same as those measured in some EU countries in 2005². Measured concentrations of Pb in Zagreb were slightly lower concentrations than the ones measured in the bark of trees in London²⁸. Comparing our results with other similar studies in Europe, particularly in neighbouring countries (Slovenia) or countries in economic transition (Romania, Turkey) measured concentrations of Pb and Cd in Zagreb were lower^{12,29–32}.

Moreover, comparing our results with the 2003 measurements of Pb and Cd in soil multiple reduction of cadmium was observed (from 3.84 mg/kg in 2003 to 0.66 mg/kg in 2007), and stagnation with a slightly higher maximum survey of lead in soil (150 mg/kg in 2007 in relation to the maximum 139 mg/kg in 2003). The reduction of Cd values is probably due to sampling variability. At the same time all of the systematic measurements of air quality showed a visible decline in metal concentration over the 10 year period¹⁸.

Conclusion

Knowing whether the vegetables grown in an urban area are safe for human consumption is of great public

REFERENCES

1. EWERS U, FREIER I, TURFELD M, BROCKHAUS A, HOFSTET-TER I, KONIG W, LEISNER-SAABER J, DELSCHEN T, Gesundheitswesen, 55 (1993) 318. - 2. HARMENS H, MILLS G, HAYES F, WIL-LIAMS P, De TEMMERMAN L, (2005) Air pollution and Vegetation. The International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops Annual Report 2004/2005. Available from: http://www.lidwala.com/wp-content/uploads/Ewwaro-DESR-Ch-9-References.pdf. - 3. GVOZDIĆ V, BRANA J, MALATESTI N, PUNTARIĆ, VIDOŠAVLJEVIĆ D, ROLAND, Coll Antropoll 35 (2011) 1135. - 4. BOŠNIR J, PUNTARIĆ D, Croat Med J, 38 (1997) 143. — 5. SINGH N, PANDEY V, MISRA J, YUNUS M, AHMAD KJ, Environ Monit Asses, 45 (1996) 9. Available from: http://www.fspublishers,org/ijab/past-issues/ IJABVOL_14_NO_6/15.pdf. — 6. BOŠNIR J, PUNTARIĆ D, ŠKES I, KLARIĆ M, ŠIMIĆ S, ZORIĆ I, GALIĆ A. Coll Antropoll 27 (2003) 31. -7. WILHELM M, WITTSIEPE J, SCHREY P, HIBIG A, KERSTING M, Sci Tot Environ, 343 (2005) 61. - 8. JÄRUP L, Brit Med Bull, 68 (2003) 167. — 9. BLANUŠA M, JUREŠA D, Arh Hig Rada Toksikol, 52 (2001) 229. - 10. De WINTER-SORKINA R, BAKKER M, van DONKERS-GOED G, van KLAVEREN JD, RIVM REPORT 310305001/2003.019. Available from: http://rivm.openrepository.com/rivm/bitstream/10029/ 8876/1/310305001.pdf. - 11. TEMMERMAN DE L, HOENIG M, J Atmos Chem. 49 (2004) 121. – 12. TÜRKDOGAN MK. KILICEL F. KA-RA K, TUNCER I, UYGAN I, Environ Toxicol Pharmacol, 13 (2002) 175. 13. KHAN S, FAROOQ R, SHAHBAZ S, KHAN MA, SADIQUE M. World Appl Sci J, 6 (2009) 1602. - 14. VOUTSA D, GRIMANIS A, SAM-ARA C, Environ Pollut, 94 (1996) 325. - 15. ROMIĆ M, ROMIĆ D, Environ Geol, 43 (2003) 795. - 16. FRANJEK I, Status report on Zagreb's Environment, City Department for Urban development, Office for ecology: Zagreb, 2006 (in Croatian). — 17. HRŠAK V, ILIJANIĆ LJ, NIKOLIĆ T, FIEDLER S, Nat Croat, 2 (1993) 109. - 18. VAĐIĆ V, Arh Hig Rada Toksikol, 57 (2006) 317. - 19. ZAGREB CITY DEPARTMENT FOR UR-BAN PLANNING AND ENVIRONMENTAL PROTECTION: Statistical health importance, especially since the consumption of such vegetables is significantly increasing. To our knowledge this is the first systematic study relating to concentrations of Pb, Cd, Hg and As in soil and vegetable samples from the gardens of Croatia's capital city or any other Croatian towns. Measured Pb, Hg and Cd concentrations in a small number of vegetable samples (4–8%) were above the allowed concentrations mainly in eastern and western part (industrial) of the city, respectively. The results revealed that the mean concentrations of the metals and metalloids in the vegetables were within the maximum allowed concentration recommended by national and EU legislation.

Regardless of the »good results« presented in this study, permanent monitoring of leafy vegetables and soil samples should be recommended as part of the unique public health measures for the city of Zagreb and Croatia in general. The higher levels of Hg in vegetables in the northern, residential part of the city have other sources which are so far unknown and must be explored.

Acknowledgement

This study is part of the project »Investigation of long term effects of war on population« by the Ministry of Science, Education and Sports of the Republic of Croatia. Analyses were performed at the Department of Health Ecology, Zagreb Institute for Public Health.

Annual report for city of Zagreb, 2005 (in Croatian). — 20. BEATTY RD, KERBER JD. Concepts, instrumentation and techniques in atomic absorption spectrometry, Norwalk, CT, Perkin-Elmer Corporation, 1993. -21. REPUBLIC OF CROATIA, Law on environmental protection for agricultural soils. Official gazette, 32 (2010). — 22. REPUBLIC OF CROA-TIA, Act on agricultural land protection from contamination. Official gazette, 16 (2005). - 23. PUSCHENREITER M, HORAK O, Plant Soil Environ, 51(2005)11. - 24. EUROPEAN COMMISION, Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs. Official Journal of the European Union, 20.12.2006. — 25. DEPARTMENT FOR ENVIRONMENT FOOD AND RURAL AFFAIRS (DEFRA), UK (2004). Mercury emissions from crematoria. Second consultation, Department for Environment, Food and Rural Affairs; Welsh Assembly Government; Scottish Executive Environment and Rural Affairs Dept. Available at: www.defra.gov.uk/corporate/consult/current.htm. - 26. KACHENKO A, SINGH B, (2004) Heavy metals contamination of home grown vegetables near metal smelter in NSW. 3rd Australian New Zealand Soils Conference, 5-9 December 2004, University of Sydney, Australia. — 27. JORHEM L, ENG-MAN J, LINDESTROM L, SCHRODER T, Commun Soil Sci Plant Anal, 31 (2000) 2403. - 28. SUZUKI K, Atmos Environ, 40 (2006) 2626. Available at: http://dx.doi.org/10.1016/j.atmosenv.2005.12.022. - 29. LÃCÃ-TUSU R, LÃCÃTUSU AR, Carpath J Earth Env Sci, 3 (2008) 115. - 30. PAN J, PLANT JA, VOULVOULIS N, OATES CJ, IHLENFELD C, Environ Geochem Health, 32(2010) 1. DOI: 10.1007/s
10653-009-9273-2. — 31. $\,$ KUGONIČ N, GRČMAN H, The accumulation of cadmium, lead, and zinc by different vegetables from Zasavje (Slovenia). In: VIHLAR B, GRILL D, GUTTENBERGER H (eds), 2nd Slovenian Symposium on Plant Physiology with international participation: Special edition, (Phyton). Horn (Austria): Apud Ferdinandum Berger & Fil, Special issue, 39 (1999) 161. - 32. KUGONIČ N, KOPUŠAR N, Phyton (Horn), 40 (2000) 117.

D. Puntarić

Zagrebačka 22a, HR 10313 Graberje Ivanićko, Croatia e-mail: dinko.puntaric1@gmail.com

KONCENTRACIJE TEŠKIH METALA I METALOIDA U POVRĆU I TLU VRTOVA GRADA ZAGREBA

SAŽETAK

Cilj ovog rada je bio određivanje koncentraciju Pb, Cd, As i Hg u zelenom lisnatom povrću i tlu na urbanom području Zagreba, te utvrditi eventualnu povezanost između onečišćenja tla i povrća. Zeleno lisnato povrće i uzeti su uzorci tla iz vrtova smještenih na periferiji grada. Koncentracije Pb, Cd, As i Hg određene atomskom apsorpcijskom spektrometrijom pokazuju da su prosječne koncentracije metala i metaloida u povrću i tlu, bez obzira na mjesto uzorkovanja, ispod maksimalnih dozvoljenih vrijednosti. Analizom je utvrđeno su koncentracije metala u samo devet uzoraka biljaka (9%) bile više od maksimalno dopuštenih vrijednostiprema nacionalnoj i europskoj legislativi (tri s višim koncentracijama Pb, jedna s većom koncentracijom Cd i pet s višim koncentracijama Hg). Koncentracije ispitivanih tvari u analiziranim uzorcima, u cjelini su niže od onih objavljenih u sličnim studijama. Na distribuciju i koncentraciju onečišćujućih tvari u povrću Zagreba, osim industrije i prometa, najveći utjecaj ima dominantni smjer vjetra.