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Garden Soil and Vegetable Pollution Assessment of the Upper Meža Valley (Slovenia)

By

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Key words: Polluted soils, vegetables, heavy metal accumulation, cadmium, lead, zinc.

Summary

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Soil pollution and accumulation of heavy metals in most common vegetables (lettuce, endive and carrot) were investigated in towns of Mežica, Žerjav and Črna in 1998. Eighteen gardens in different distances from the lead smelter in Žerjav were included in the field experiment. Cd, Pb and Zn were measured in topsoil samples, unwashed and washed edible green parts of lettuce and endive as well as roots of carrot. Results confirmed that soils and vegetables are still contaminated with Pb, Cd and Zn in the wide area of the Upper Mežica Valley. Grounds are strongly polluted with heavy metals (4.99 ± 6.92 mgkg^{-1}, 1496.11 ± 1071.02 mgkg^{-1}, 498.22 ± 546.0 mgkg^{-1} for Cd, Pb and Zn, respectively) and leafy vegetables on these grounds have a high Cd content (6.05 ± 5.83 mgkg^{-1}, 4.05 ± 4.32 mgkg^{-1}, 3.62 ± 4.97 mgkg^{-1}, 2.42 ± 2.07 mgkg^{-1} for unwashed endive, unwashed lettuce and washed endive, washed lettuce, respectively).

Introduction

The Upper Meža Valley has been exposed to active lead ore mining and smelting activities since the 15th century. Soil in the Upper Meža Valley is highly polluted with heavy metals, especially with Pb, Cd and Zn (PRPIĆ-MAJIĆ 1996). In 1989 technology of lead processing changed and the primary raw material (lead sulphide ore) was replaced by a secondary raw material (old lead storage batteries). No single research about soil and vegetable pollution has been performed since than. The main objective of our study was to determine quality of the soil and commonly grown vegetables at gardens in different distances from the main pollu-

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tion source (the lead smelter at Žerjav).

The uptake of heavy metals and their compounds by plants depends on concentrations and solubility of heavy metals in soils, on soil properties and plant species (BERGMANN 1992). Althought soil concentrations of Cd, Pb and Zn are high, total metal content does not necessarily mean that the amount of metal is available to plants (ALLOWAY 1988). Rhizosphere is a biologically active zone in the vicinity of growing plant roots, in which micro-organisms and root exudates can modify the forms of metals. Highly labile cations, such as Cd, move to the root in the soil solution by diffusion and mass flow. The root absorption of more strongly sorbed ions, such as Pb, depends to a greater extent on root interception than movement in the soil solution (JARVIS 1981). Plants can also derive significant amounts of some elements through foliar absorption (ALLOWAY 1990).

Materials and Methods

The field experiment with lettuce (*Lactuca sativa*), endive (*Cichorium endiviae*) and carrot (*Daucus carota*) as test plants was carried out in 18 locations in different distances from pollution sources in the Upper Meža Valley. After growing in the greenhouse 15 plantlets of endive were transplanted to each location. Carrots and lettuce were sown directly on the experimental sites. Each species occupied 3 m^2 at each site. 12 - 15 examples of each species were sampled. Different parts of plants were separated and homogenized. Heavy metal concentrations were measured in washed roots of carrot, washed and unwashed leaves of endive and lettuce. Soil samples were taken from topsoil (0 - 20 cm). An average soil sample from each garden was prepared as a composite of 18 sub-samples taken from an area 250 m^2 in size (ISO 10381-1). Soil samples were homogenized and ground by hand in a ceramic grinder, then passed through a 2 mm plastic sieve before the analyses. For the analyses of metal content the samples were ground further in an agate mill for 10 minutes, then passed through 250 µm sieve. Heavy metals concentrations in soil were determined using flame and electrothermal atomic absorption spectrometric methods (ISO 11466, ISO/DIS 11047). pH was measured in 0.1 M KCl solution, the content of organic matter by the Walkley-Black method and soil texture by pipette method (JANITZKY 1986). Plant tissues were dried at 36 °C and ground in an agate mortar. The acid dissolution technique with microwave heating system was used for wet digestion of samples (250-500 mg dry weight plant samples were treated with 65 % HNO_3). Electrothermal technique was used for the determination of Cd and Pb, while flame atomic absorption spectrometry was used for the determination of Zn content in plants.

Results and Discussion

Wide range of heavy metals concentrations were determined in soil from the Upper Meža Valley. In almost all locations concentrations of Pb, Cd and Zn exceed critical values according to OFF. GAZ. REP. SLOV. 1996 which are 530 $mgkg^{-1}$, 12 $mgkg^{-1}$ and 720 $mgkg^{-1}$, respectively. Soil parameters in the soil from Meža Valley, especially pH, do not suggest high bioavailability of heavy metals for plants, while the Pb, Cd and Zn are much more soluble at pH 4 - 5 than in the range of 5 - 7 (BRUMMER & HERMS 1983). Generally availability of metal decreases as the pH level rises and the contents of clay and humic increase (MENGEL & KIRKBY 1987). Among 18 gardens the outlier in Pb levels appeared at a site near the landfill Polena in Mežica, where the concentration in average soil sample was measured as 2830 mg

Pb/kg. The highest Pb level in soil was measured in Žerjav (4470 mg/kg), where the critical Pb level in soil is exceeded for eightfold. After the elimination of these sites from the statistical processing, the correlation coefficient (Pb level: distance from smelter) increased to -0.63 ($P<0.05$). Cd levels in soil exceed critical value on both above mentioned sampling sites approximately for twofold (Table 1).

Table 1. Chemical and physical properties of the soil layers on the depth 0 - 20 cm (DW = dry weight).

		pH_{KCl}	org. matter (%)	clay (%)	Cd ($mgkg^{-1}DW$)	Pb ($mgkg^{-1}DW$)	Zn ($mgkg^{-1}DW$)
Official	Limit values	/	/	/	1	85	200
journal	Warning value	/	/	/	2	100	300
RS 68/96	Critical values	/	/	/	12	530	720
Locations / Distance from lead smelter (km)							
1	0.3	6.8	12.1	3.9	19.8	4470	704
2	0.4	6.5	11.3	4.5	15.7	3350	736
3	1.1	6.5	11.0	10.7	2.52	1890	557
4	1.4	7.0	8.7	16.1	1.28	925	172
5	1.5	7.0	10.0	6.2	1.42	1190	160
6	1.7	6.5	7.7	4.6	5.91	1950	699
7	1.8	7.0	9.3	7.5	1.34	897	351
8	1.8	6.8	6.7	12.7	1.34	734	333
9	3.0	6.7	21.2	4.1	4.89	1710	624
10	3.5	6.7	14.0	5.8	3.15	1410	535
11	4.0	6.5	29.7	3.2	23.0	2830	785
12	4.5	6.8	17.0	5.1	1.55	898	475
13	4.6	7.0	13.5	5.1	1.46	1030	697
14	4.8	7.1	11.5	4.7	1.89	947	558
15	4.9	6.9	10.5	1.9	0.89	597	307
16	5.2	6.9	19.9	3.8	1.41	593	444
17	5.2	6.6	17.0	6.8	1.44	936	582
18	5.9	6.8	18.1	14.4	0.89	573	249

Legend to locations: 1 Žerjav Fajmut, 2 Žerjav Petre, 3 Mušenik – Haberman, 4 Rudarjevo polje, 5 Mušenik – Odbojnik, 6 Črna -Center, 7 Črna - Štrucl, 8 Lampreče, 9 Pristava, 10 Head quarter of the mine, 11 Landfill Polena, 12 Primary school Mežica, 13 Ob Meži, 14 Vivodovo, 15 Mrvovo, 16 Ekonomija, 17 Senčna vas, 18 Reht.

Different plant species differ in their heavy metal uptake capacities. They are enriched with heavy metals in various plant organs, depending on metal availability, concentration and mobility (HUDNIK & al. 1994). The highest concentrations of heavy metals were observed in edible green parts of lettuce and endive (Table 2).

The average contents of Cd and Pb in unwashed lettuce exceed ($P<0.05$) officially determined maximum level (0.3 and 3.0 mg/kg for Cd and Pb, respectively; OFF. GAZ. SOC. FED. REP.YUG. 59/8). We revealed that leafy vegetables accumulate higher amounts of Cd in comparison with Pb. About 87 % – 99 % of Pb can be reduced by washing. However, only 40 % of Cd can be washed off. The officially determined maximum level for Cd was exceeded on all gardens (100 %)

and on 11 experimental sites (61 %) for washed lettuce and endive, respectively. The results reveal that Cd content in endive leaves decreased with the distance from lead smelter in Žerjav. The linear correlation coeficient is -0.63 and -0.72 for unwashed and washed endive, respectively ($P<0.05$). In carrot, the officially determined maximum level for Cd was exceeded on 8 experimental sites (44 %), in spite that the average Cd and Pb levels in carrot did not exceed the allowed levels ($P<0.05$). The linear correlation coeficient (-0.64) showed that Pb content in carrots decreased with the distance from Žerjav.

Table 2. Content of Cd, Pb and Zn in vegetables grown on polluted soils ($mgkg^{-1}$ DW).

		Cd ($mgkg^{-1}$DW.)					Pb ($mgkg^{-1}$DW.)					Zn ($mgkg^{-1}$DW.)				
Official journal SFRJ 59/83		0,3					3					/				
Locations / Distance from lead smelter (km)		E un.	E wa.	L un.	L wa.	C	E un.	E wa.	L un.	L wa.	C	E un.	E wa.	L un.	L wa.	C
1	0.3	20.8	17.4	10.3	5.7	0.11	250	21.9	392	13.6	2.1	201	197	168	80.3	23.1
2	0.4	15.8	11.6	16.6	8.6	0.11	53.6	6.8	490	4.5	1.0	210	152	309	86.5	23.0
3	1.1	8.5	8.2	2.7	1.3	1.4	10.3	1.2	44.6	1.2	0.73	115	110	146	69.7	31.3
4	1.4	6.6	4.9	/	3.5	0.06	36.3	1.5	/	1.4	0.22	49.8	35.1	/	43.6	29.2
5	1.5	4.8	3.4	0.82	0.67	0.08	4.0	0.40	246	1.1	1.0	35.3	49.6	67.7	57.7	47.7
6	1.7	10.5	9.9	/	4.5	2.3	13.1	1.6	/	3.0	0.77	124	105	/	67.4	31.0
7	1.8	2.8	2.6	2.1	1.8	0.33	12.1	1.8	21.4	2.0	0.14	43.1	33.0	69.4	51.8	27.2
8	1.8	0.91	0.90	1.4	0.94	0.10	1.0	1.5	2.3	2.3	0.12	32.8	21.0	64.1	39.5	29.3
9	3.0	4.6	2.7	4.2	1.3	0.07	3.2	0.01	170	1.4	0.26	61.9	56.0	139	104	33.2
10	3.5	2.6	0.3	/	3.6	0.99	6.1	3.6	/	1.6	0.94	43.2	56.3	/	95.0	31.6
11	4.0	15.1	1.7	/	1.1	1.2	40.8	5.2	/	0.56	1.7	428	423	/	210	126
12	4.5	2.4	0.2	/	2.0	0.41	5.0	2.1	/	0.76	0.19	61.7	41.3	/	33.3	20.9
13	4.6	3.1	0.3	2.2	2.1	< 0.05	2.9	2.8	17.2	1.1	0.24	86.2	70.3	90.5	47.6	45.4
14	4.8	1.0	0.5	4.6	1.5	0.42	22.2	6.0	3.2	0.6	0.34	222	75.2	90.4	53.3	33.4
15	4.9	2.1	0.2	1.9	1.9	0.54	4.8	1.9	1.6	0.7	0.08	57.9	35.3	59.9	43.1	21.0
16	5.2	3.5	0.2	3.6	1.0	0.15	1.5	1.8	1.6	0.56	0.05	1.5	1.8	1.6	0.56	0.05
17	5.2	1.7	0.1	1.4	1.0	< 0.05	2.2	2.8	1.8	0.70	0.08	74	43.5	66.0	33.3	25.1
18	5.9	2.1	0.1	1.3	1.0	0.33	2.8	1.5	1.8	0.37	0.07	58.8	40.5	47.6	41.3	14.8

Legend: E un.- Endivia unwashed; E wa.- Endivia washed; L un.- lactuca unwashed; L wa.- Lactuca washed; C- carrot; Locations: 1 Žerjav Fajmut, 2 Žerjav Petre, 3 Mušenik – Haberman, 4 Rudarjevo polje, 5 Mušenik – Odbojnik, 6 Črna -Center, 7 Črna - Štrucl, 8 Lampreče, 9 Pristava, 10 Head quarter of the mine, 11 Landfill Polena, 12 Primary school Mežica, 13 Ob Meži, 14 Vivodovo, 15 Mrvovo, 16 Ekonomija, 17 Senčna vas, 18 Reht.

Our study confirmed that soils and vegetables in the wide area of the Upper Meža Valley are still contaminated with Pb, Cd and Zn. The conclusion is consistent with ascertainment of heavy metal level in roe deer tisues (POKORNY & RIBARIČ-LASNIK 2000). The heavy metal burdens are highest in Žerjav (where lead smelter is located) and near the landfill in Mežica. Contaminated soils and probably industrial emissions are the main sources of pollution with heavy metals in edible plants in the area. Unfortunately, there is no data of the air pollution in the region. However, leafy vegetables represent a potential hazard for human beings considering Cd uptake.

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