Phyton (Austria) Special issue: "Plant Physiology"	**Vol. 39**	Fasc. 3	(161)-(165)	30. 11. 1999

The Accumulation of Cadmium, Lead and Zinc by different Vegetables from Zasavje (Slovenia)

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K e y w o r d s : Polluted soils, cadmium, lead, zinc, accumulation.

S u m m a r y

KUGONIČ N. & GRČMAN H. 1999. The accumulation of cadmium, lead and zinc by different vegetables from Zasavje (Slovenia). - Phyton (Horn, Austria) 39 (3): (161) - (165).

Zasavje has been exposed to mining and electricity production in last two centuries. Except by emissions from the Trbovlje Thermal Power Plant environment is also polluted by other kinds of industry, which is situated in narrow valleys. In our research soil pollution and accumulation of heavy metals in most common vegetables were investigated in Zagorje ob Savi. Eight gardens in different distances from pollutant sources were included in the field experiment. Samples of topsoil, unwashed and washed edible green parts of endive (*Cichorium endiviae*) and roots of carrot (*Daucus carota*) were sampled and analyzed for Pb, Cd and Zn. Heavy metal concentrations in soil and plants were determined using flame and electrothermal atomic absorption spectrometric methods. The results of the soil analysis showed that the soil is not polluted with heavy metals. In contrast, endive leaves and carrot roots from all gardens accumulated high concentrations of Cd. Concentrations of Pb in washed and unwashed leaves of endive indicated that plants are affected by emissions from industry. The concentrations of Cd in analyzed plants are the highest, because it is the most mobile heavy metal.

I n t r o d u c t i o n

Agricultural soils are exposed to trace metals at a much higher rate than in previous periods. Antropogenic trace metals enter the soils by aerial deposition, pesticide and fertilizer application, waste utilization, dredged sediment disposal and river and irrigation waters (SALOMONS & al. 1995). Some elements like Cd, Pb, Zn, Hg, Ni, As, Mn, Cr, Co, Se are phytotoxic at high concentrations, because of

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their affinity to bind into complex with parts of biologically active molecules (LOBNIK & HRUSTEL-MAJCEN 1989).

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). The availability of heavy metals is strongly influenced by the clay and humus content, cation exchange capacity, pH and ionic activity. Generally availability of metal decreases as the pH level rises and the contents of clay and humic increase (MENGEL & KIRKBY 1987). Plants can also derive significant amounts of some elements through foliar absorption (ALLOWAY 1990). Different plant species differ in their heavy metal uptake capacities and are enriched with heavy metal in various plant organs, depending on metal availability, concentration and mobility (HUDNIK & al. 1994). The plants where the roots and leaves are used for human or animal food are critical concerning the accumulation of heavy metals. Especially salad vegetables are exposed to deposition from the polluted air (ZUPAN & al. 1995). The accumulation of cadmium, lead and zinc in edible green parts of endive and roots of carrot were determined in the field experiment.

Materials and Methods

The field experiment with endive (*Cichorium endiviae* -Eskariol zelena) and carrot (*Daucus carota* - Nantes) as test plants was carried out in 8 locations in different distance from pollutant sources in Zasavje. Seedlings of endive were grown in the greenhouse, than 15 plantlets were transplanted to each location. Carrots were sown directly on the experimental sites. Each species occuped 3 m^2 at each site. For each test species 12 – 15 plants were sampled. Individual parts of plants were separated and homogenous samples were prepared. In washed roots of carrot, washed and unwashed leaves of endive heavy metal concentrations were measured in three replicates. Soil samples were taken from topsoil (0 - 20 cm). An average soil sample from each sampling site was prepared as a composite of 18 sub-samples taken from an area 250 m^2 in size (DIN ISO 10381-1 1996). Soil samples were homogenized, and ground by hand in a ceramic grinder, then passed through a 2 mm plastic sieve before soil analyses (SIST ISO 11464 1994). For the analysis of metals 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 1995, ISO/DIS 11047 1995). Methods used for analysis of other soil parameters were: pH was measured in 0.1 M KCl solution, available, the content of organic matter by the Walkley-Black method and soil texture by pipette method (JANITZKY 1986). Plant tissue samples were dried at 40°C and ground in a agate mortar. 250-500 mg DW plant samples were treated with 65 % HNO_3 acid. Electrothermal technique was used for the determination of Cd and Pb, and flame atomic absorption spectrometry for the determination of Zn content in plant after the acid dissolution technique with microwave heating.

Results and Discussion

Lead, cadmium and zinc content in soil from all locations did not exceed critical values according to OFF. GAZ. REP. SLOV. 68/98 1996 which are 530 $mgkg^{-1}$, 12 $mgkg^{-1}$, 720 $mgkg^{-1}$ respectively (table 1). Heavy metal concentrations

in soil and results of analyses of other parameters did not suggest high heavy metals accumulation in plants.

Table 1. Chemical and physical properties of the surface soil layers (0-20 cm).

Locations	pH_{KCl}	org. mat. %	clay %	Cd $mgkg^{-1}$	Pb $mgkg^{-1}$	Zn $mgkg^{-1}$
1. Zelena trava	7.1	8.4	20.0	0.61	57.6	112
2. Leskovca	6.8	10.3	7.4	0.47	51.1	110
3. Kraj	6.6	10.0	14.3	0.44	51.6	110
4. Javor	6.8	10.5	25.1	0.69	53.8	141
5. Dolenja vas	7.1	3.5	19.2	0.17	23.8	68.2
6. Loke	7.0	17.7	13.0	0.44	10.0	108
7. Obrezija	6.5	12.5	13.9	0.18	35.1	76.6
8. Selo	6.7	10.5	17.0	0.13	31.1	77.5

Table 2. Pb, Cd and Zn content in washed and unwashed endive and carrot.

Location	Vegetable	Cd $mgkg^{-1}$	RSD %	Pb $mgkg^{-1}$	RSD %	Zn $mgkg^{-1}$	RSD %
1. Zelena trava	endive - washed	0.33	±9	1.2	±7.0	34.8	±5.0
	endive - unwashed	0.42	±2.7	3.1	±10.0	31.2	±5.0
	carrot	0.3	±2.5	<0.1	/	10.3	±5.0
2. Leskovca	endive - washed	0.34	±3.2	1.1	±4.2	29.3	±5.0
	endive - unwashed	0.42	±1.2	1.6	±4.3	28.6	±5.0
	carrot	0.4	±8.8	0.5	±1.5	<10.0	/
3. Kraj	endive - washed	0.4	±2.4	1.1	±7.3	24.4	±5.0
	endive - unwashed	0.6	±1.4	1.2	±8.3	26.8	±5.0
	carrot	0.4	±0.5	<0.1	/	13.5	±5.0
4. Javor	endive - washed	0.78	±10.3	1.4	±3.6	48.4	±5.0
	endive - unwashed	0.81	±1.2	1.5	±6.6	46	±5.0
	carrot	0.8	±1.7	<0.1	/	16.5	±5.0
5. Dolenja vas	endive - washed	0.41	±2.9	1.1	±6.0	24.6	±5.0
	endive - unwashed	0.44	±1.6	2.9	±10.0	27.1	±5.0
	carrot	0.4	±7.1	0.1	±10.0	0.1	±5.0
6. Loke	endive - washed	0.33	±1.4	1.1	±1.0	0.6	±5.0
	endive - unwashed	0.37	±1.7	3.5	±10.0	1.1	±5.0
	carrot	0.6	±4.3	<0.1	/	0.2	±5.0
7. Obrezija	endive - washed	0.19	±3.7	1.1	±4.0	0.1	±5.0
	endive - unwashed	0.21	±2.1	3.2	±2.4	0.4	±5.0
	carrot	0.3	±0.5	0.1	±10.0	0.1	±5.0
8. Selo	endive - washed	1.34	±3.3	1.1	±1.0	2.2	±5.0
	endive - unwashed	1.41	±3.7	2.9	±3.4	3.6	±5.0
	carrot	0.6	±3.1	0.1	±6.6	1	±5.0

The analysis of plant parts showed different picture (Table 2). All samples except one had concentration of Cd over officially determined value for vegetables

(0.3 $mgkg^{-1}$ DW, OFF. GAZ. SOC. FED. REP. YUG. 59/83). Endive was the most contaminated in Selo where the concentration of Cd in washed and unwashed leaves was over 1 mg/kg.

There is no great differences between Cd content in washed and unwashed leaves of endive and roots of carrot. Cadmium is most mobile in acidic soils within the range of pH 4.5 to 5.5, whereas in alkaline soil Cd is rather immobile. A great proportion of the Cd is known to be accumulated in root tissues, even when Cd enters the plant via foliar systems (KABATA PENDIAS & PENDIAS 1984).

Analyses of lead concentrations showed that only the unwashed samples of endive leaves exceeded officially determined maximum level of lead in vegetables (3 $mgkg^{-1}$ DW, OFF. GAZ. SOC. FED. REP. YUG. 59/83 1983). Lead concentrations in washed and unwashed leaves of test plant showed that plants were affected by atmospheric deposition. According to ALLOWAY 1990 the lead contamination of plants was generally only external while aerosol-deposited Pb particles did not penetrate the cuticle of higher plants, but tend to adhere to the surface of leaves. Contamination levels can even be reduced by 90% by washing (BERGMANN 1992).

Ease of removal of Pb by washing suggests that the metal was largely a superficial deposit on the leaf surface. In the contrast the small fraction of Cd that can be washed off indicates a greater leaf penetration.

Acknowledgments

This study has been financially supported by the local community Zagorje ob Savi. Thanks to J. RODE for his help with English translation.

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