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Lead, Mercury, and Nickel in Grapevine, *Vitis vinifera* L., in Polluted and Nonpolluted Regions

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The environment surrounding electric power plants is exposed to pollution by diverse pollutants, heavy metals and radio-nuclides being most prominent for their toxic effects. That is why agricultural products safety is brought into question, especially that of fruits and vegetables produced in the zone of air polluters, such as these power plants. Coal utilized for fuel in steam power plants is a major cause of increased content of heavy metals in soil and plants (Sawidis et al.2001; Cicek and Koparal 2004). After burning of coal, heavy metals can be found in slag (Al, Ba, Co, Fe, Mn, K), in flying ash that condenses on surfaces of small objects (As,Cd,Cu, Pb, Zn), in both these forms (Cr, Ni, U and V), or in the form of gas (Hg), (Klein et al. 1979).Crops grown in the vicinity of power plants use their above-ground organs, primarily leaves, to store up heavy metals from the air and root system to store them up from soil solution. Uptake of heavy metals in plant tissues can occur either via roots or leaves and content of metal ions in above-ground plant organs is not always linearly correlated with their content in the soil (Reimann et al.2001; Chojnacka et al.2005).

Consumption of fruits with increased content of heavy metals can cause cancer, neurological and nephritic diseases. A volume of epidemiological studies evidenced a substantial increase in cancer incidence in regions where depositions of heavy metals and other toxic matter from the air is present (Boffetta 1993; Hayes 1997; Türkdogan et al.2002).

MATERIAL AND METHODS

The first location (L1) where soil samples and grapevine plant parts were taken from is a vineyard in a suburban zone of the town Obrenovac. The steam power plant “Nikola Tesla” (TENT) A of 520MW is situated about 3-4 km away from the town and L1, while the TENT B of 620MW is 15 km from the town. The TENT A and TENT B are at the town zone borderline and are a steady source of the emission of gases (SO_2, NO_x, CO) and smoke particles which are concentrates of heavy metals and radio-nuclides. On the basis of data provided by the Belgrade City Institute for Health Protection, the emission of smoke particles from the new generating units of the TENT B exceeds by 1.2-1.9 times the lawfully permissible level, while in the old generating units of the TENT A plant the levels rise as high

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as 27 times the permitted level. Apart from the particle emission from chimneys, air and ground-waters are polluted by ash dumps from the steam power plants, where ash and slag particles are dispersed by wind throughout the environment. It is thought that between 17,000 and 30,000 tons of ash and slag, containing high concentrations of heavy metals, are dumped in this area daily, Sabovljevic (2003). Average values for ash amount from the chimneys of steam power plants A and B and from their dumps found during the 1992-2002 period for the town of Obrenovac and its environment are as high as 500 $mg/m^2/day$. The second location (L2) where samples were taken is a vineyard in a village situated about 15 km away from the Ub township whose environment is assumed to be free from polluters.

Soil samples were taken at depth from 0 to 30 cm on both location, as well as samples of vine organs (*Vitis vinifera*) from vine interspecies of the Seyve Villard 18-315 hybrid which had not been treated during growth period to avoid heavy metals storing from pesticides. Six samples were taken each from the vine roots, shoots, leaves and berries, each sample weighing 100 g. Root sample consisted of root hairs and branches 1-5 mm thick, collected from the depth of 20-30 cm. Leaves were collected from middle shoots from both row sides; middle shoot portions were also taken as a sample of one-year old mature vine. Bunch fragments containing several mature berries with a part of peduncle were taken from various parts of the row. After collection, samples were water washed to remove soil and dust debris.

All vine samples were prepared in identical way. The preparation procedure consisted of drying process at 60 °C during 6 hours, and after that of grinding and homogenizing the material. Digestion of samples was then conducted with nitric acid and perchloric acid, where the amount of 0.5g of samples was cooked for 2 hours with 10ml of concentrated nitric acid, and thereafter perchloric acid was added until completely carried out dissolution.

Soil samples were prepared with standard method AOAC 971.21, by digestion of samples (5g) during 1h in the solution of 25ml 18N H_2SO_4 i 20ml 7N HNO_3. After digestion, 1ml 2% Na-molybdate was added, and than solution was filtered. The filtrate was treated with mixture of concentrated HNO_3 and $HClO_4$ on the same way as plant material.

Hg was determined by the CV-ASS (Cold Vapour Atomic Absorption Spectroscopy) technique based on modified EPA 200.9 and EPA 245.1 methods using Perkin-Elmer 5000 MHS-1. Elements Pb and Ni were determined by the GF-AAS (Graphite Furnace Atomic Absorption Spectroscopy) technique on the Perkin-Elmer 5000 HGA 400/300 device. All results are presented in mg/kg of dry matter.

The analysis of experimental results was performed by descriptive and analytical statistics using *Statistica* 5 software package (StatSoft, Inc. 2005). Of central tendency indicators, arithmetic mean and median were calculated. Data variability was quantified via variation interval, standard deviation and coefficient of variation. Reliability intervals were also determined, covering the 0.95 probability average content of analysed heavy metals in soil and plant organs at studied locations. Homogeneity of variances was checked by Bartlett and Levenes test, while harmonization of data distribution with a normal distribution model by tests given in the software used. Testing of differences between treatments was carried out using t-test, LSD-test, analysis of variance method, Mann-Whitney test, and Kruskal-Wallis test.

Table 1. Average content of Pb, Hg and Ni in the soil (mg/kg).

Location	Pb	Hg	Ni
L1	25,17	0,040*	83,19*
L2	23,58	0,012	29,00
mal*	100	2,0	50,0
lsd 0,05	3,3523	0,0262	3,7270

*mal - maximum allowed level - Values prescribed by Regulation of Serbia on maximally allowed contents poisonous substances in soil (Official Register of Serbia, N° 23/94)

RESULTS AND DISCUSSION

The soil at L1, which is more exposed to aerial pollution than L2, mostly had increased heavy metal content. The proximity of the steam power plant appears to have caused a higher Hg content at L1 compared to L2 (respectively 0.04 mg/kg and 0.012 mg/kg), well below the limit prescribed by Serbian law (2 mg/kg). Ni content was also higher at L1 than at L2 (83.2 mg/kg compared to 29 mg/kg), and also considerably over the limit proscribed by law (50 mg/kg). There were no difference in the soil Pb content between sites (25.2 mg/kg and 23.6 mg/kg, respectively for L1 and L2). This was below the maximum content permitted by law, which is 100 mg/kg of Pb, (table 1).

The lowest Pb content was found in grapevine shoots at L2 (0.12 mg/kg) and the highest content (4.07 mg/kg) was also found in shoots, but at L1. The average Pb content ranges between 0.86 mg/kg in the L2 leaf and 2.49 mg/kg in the L2 root. The determined Pb leaf content values are at the low end of the range (0.1-55 mg/kg) that Cicek et al. (2004) determined in leaves from woody perennials growing in the proximity of the Tuncbilek power plant in Turkey, and are well below the critical value of 30 mg/kg of Pb in plant organs as determined by the same authors.

The studied locations differ significantly in Pb content present in all organs studied simultaneously. At L1 statistically significantly higher Pb content was found in leaves and in a shoots and grape significantly higher Pb content than at L2. The Pb contents found in various plant organs, taken from L1 do not differ statistically, except for leaf where they are significant compared to grapes. In the L2 plants there are significant differences in Pb content in a root compared to a shoot, grape and leaf, but the difference is the result of considerably higher Pb content in plant root than in other plant organs. This can be the outcome of specific soil properties at L2, which caused higher Pb absorption by the root (table 2).

Table 2. Main statistical indicators of lead content (mg/kg) in grapevine organs.

Location	Organ	Arithmetic mean	Reliability interval (0.05)	Variation interval	Standard deviation	Coefficient of variation (%)
L1	Root	2.15	1.29-3.01	0.66-2.94	0.82	38.0
	Shoot	2.40	1.08-3.72	1.09-4.07	1.26	52.4
	Berry	1.81	1.64-1.97	1.57-1.97	0.15	8.5
	Leaf	2.65	1.89-2.46	1.69-2.89	0.27	12.6
L2	Root	2.49	1.49-3.48	1.10-3.95	0.95	38.2
	Shoot	0.97	0.51-1.43	0.12-1.37	0.44	45.1
	Berry	1.22	1.16-1.28	1.17-1.30	0.06	5.0
	Leaf	0.86	0.15-1.57	0.22-1.80	0.68	78.9

Lsd 0.05= 0.815

Table 3. Main statistical indicators of mercury content (mg/kg) in grapevine organs.

Location	Organ	Arithmetic mean	Reliability interval (0.05)	Variation interval	Standard deviation	Coefficient of variation (%)
L1	Root	0.29	0.00-1.15	0.27-1.71	0.57	59.5
	Shoot	0.25	0.27-0.34	0.26-0.36	0.03	11.1
	Berry	0.30	0.05-0.99	0.20-1.32	0.45	86.8
	Leaf	0.32	0.19-0.49	1.19-0.60	0.14	41.9
L2	Root	0.07	0.00-0.17	0.02-0.26	0.09	132.1
	Shoot	0.12	0.03-0.20	0.004-0.2	0.08	66.9
	Berry	0.13	0.10-0.15	0.09-0.15	0.02	16.8
	Leaf	0.06	0.02-0.10	0.001-0.1	0.04	58.9

Lsd 0.05=0.311

Table 4. Main statistical indicators of nickel content (mg/kg) in grapevine organs.

Location	Organ	Arithmetic mean	Reliability interval (0.05)	Variation interval	Standard deviation	Coefficient of variation (%)
L1	Root	3.52	2.71-4.33	2.46-4.37	0.77	22.0
	Shoot	3.40	1.41-5.38	0.94-6.67	1.89	55.6
	Berry	2.16	1.35-2.98	1.40-3.28	0.78	36.0
	Leaf	11.82	2.74-20.9	6.91-29.4	8.66	73.2
L2	Root	9.05	5.63-12.5	6.62-15.1	3.26	36.0
	Shoot	2.47	1.20-3.74	0.29-3.92	1.21	49.1
	Berry	1.77	1.62-1.92	1.63-2.04	0.14	8.1
	Leaf	9.54	8.46-10.6	8.01-10.8	1.03	10.8

Lsd 0.05=3.977

In analyzed samples, minimum Hg content (0.001 mg/kg) was found in the L2 leaves, while the maximum content was found in the L1 leaves (Table 3). Hg content in all examined grapevine organs at both locations is within the normal range (Gardea-Torresday et al. 2005), which is 0.1-9.5 mg/kg. Our Hg values are also below those determined by Samecka-Cymerman et al. (1999) in the woody plant tissues in Wroclaw, Poland, in the conditions of aerial pollution. Hg concentration was significantly higher at L1 than at L2 in general and taken for individual plant organs. Within the locations themselves, significant difference was not found.

The Ni content varied in a broad range, from 0.29 mg/kg in the L2 shoots to 29.40 mg/kg at the L1 leaves. The lowest average value was 1.77 mg/kg and refers to the L2 grapes. On average, the L1 leaves had a highest Ni content (11.82 mg/kg). At both locations the determined Ni content in grapevine organs was within the normal values for fruit and vegetables (1-10 mg/kg), as reported by Herrick et al. (1990). The Ni content in leaf was considerably below 53 mg/kg that was found by Türkdogan et al. (2002) in the Turkish areas that reportedly have increased occurrence of cancer. The markedly high Ni content in the L1 soil was not associated with an increased content of this element in the grapevine roots grown in this area; on the contrary, Ni was significantly higher in the grapevine roots from the non-polluted L2 soil, which indicates that the contamination of above-ground vine parts in L1 originates from air pollution. Ni content differed between the examined grapevine organs: the L1 leaf Ni content was higher than in berries, shoots and roots. In the L2 grapevine organs, significant differences were found in Ni content but in favour of the leaves.

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