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Assessment of Heavy Metal and Pesticide Levels in Soil and Plant Products from Agricultural Area of Belgrade, Serbia

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Abstract This study was aimed to assess the levels of selected heavy metals and pesticides in soil and plant products from an agricultural area of Belgrade, Serbia and to indicate possible sources and risks of contamination. Soil, vegetable, and fruit samples from the most important agricultural city areas were collected from July to November of 2006. Metal contents were determined by atomic absorption spectrometry, whereas pesticide residues were analyzed by gas chromatography–mass spectrometry after extraction performed using solid-phase microextraction technique. Soil characterization based on the determination of selected physical and chemical properties revealed heterogeneous soils belonging to different soil groups. The concentrations of lead, cadmium, copper, and zinc in soil samples do not exceed the limits established by national and international regulations. Residues of the herbicide atrazine were detected in three soil samples, with levels lower than the relevant limit. The presence of other herbicides, namely prometryn, chloridazon, acetochlor, flurochloridone, and napropamide, was registered in some soil samples as well. Among the insecticides investigated in the soil, fenitrothion and chlorpyrifos were the only ones detected. In most of the investigated vegetable samples from the Obrenovac area, Pb and Cd contents are higher in comparison with the maximum levels, indicating the emission of coal combustion products from local thermal power plants as a possible source of contamination. Residue levels of some herbicides and insecticides (metribuzin, trifluralin, pendimethalin, bifenthrin, chlorpyrifos, and cypermethrin) determined in tomato, pepper, potato, and onion samples from Slanci, Ovča, and Obrenovac areas are even several times higher than the maximum residue levels. Inappropriate use of these plant protection products is considered to be the most probable reason of contamination. Because increased levels of heavy metals and pesticide residues found in plant products could pose a risk to consumers' health, their continual monitoring before product distribution to city markets is indispensable.

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Most food products contain natural or synthetic chemicals that might represent a health hazard to the consumer. Hence, regular and stringent food quality control, based on Codex and other Food Agriculture Organization/World Health Organization (FAO/WHO) food standards, with an emphasis on pesticide residue and heavy metal contamination, is going to become an imperative. As a consequence of an outstanding concern for human health, programs dealing with monitoring of air, water, and soil contamination have been performed throughout the European countries. Environmental monitoring projects, including assessment of the content of harmful substances in soil as well as pesticide residues in food commodities of plant origin, soil, and water, have been carried out in Serbia also.

Systematic monitoring of the city of Belgrade environment (air, soil, drinking and river water quality, communal noise, and radioactivity) has been regularly organized by

the Secretariat for Environmental Protection of the City of Belgrade Assembly, but there is no systematic and comprehensive assessment of contamination of agricultural soil and plant products distributed to city markets. Hence, to establish a long-term strategy of agricultural product quality control, Project: Toxic Elements and Pesticides in Agricultural Land and Plant Products in the Belgrade Area was approved by this Secretariat in 2006. During the first research phase, samples of agricultural soils and representative plant products, mostly fruit and vegetables raised on private farms and distributed to city markets immediately after gathering, were collected from selected city locations and analyzed to determine the content of pesticides and heavy metals. The obtained results are discussed with the aim of assessing the level and possible sources of contamination, as well as potential risks to human health. In addition, some forthcoming activities necessary to provide food safety are proposed.

Materials and Methods

Sample Collection

Agricultural land on the territory of Belgrade, with various types of agricultural practices, including fruit, vegetable, and grain production, covers an area of 223,478 ha. The studied city agricultural areas are depicted in Fig. 1. Agricultural soil samples (24) were collected in October 2006. Sampling sites were determined in advance to get representative samples of the main soil groups. Soil samples from plastic sheds were included in the study as well.

Soil sampling was done in accordance with the standard ISO 10381-2 (ISO 2002). Because only agricultural soil was considered in this study, soil samples were taken from a 0–30-cm depth representing both the plough layer and the root zone. Five increments of a 1-kg soil sample were taken using diagonal pattern in a 50-m-diameter area, and a composite sample was formed.

Representative vegetable and fruit samples (21), from the areas given in Fig. 1, were collected in July and August 2006. Vegetables cultivated both in open fields and plastic sheds were included in the study. Cabbage, tomato, pepper, potato, cucumber, onion, peach, and apricot samples were collected according to relevant EU protocols (CEC 2002).

Chemicals

Residue-grade organic solvents (J.T. Baker, USA) were used for pesticide residue determinations. Pesticide standards, purchased from different manufacturers, were of 90.05–99.9% purity. Atomic absorption standard solutions (J.T. Baker, USA; 1000 μg/mL concentration, 99.8% purity) and inorganic chemicals of trace analysis grade were used in heavy metal analyses. All the experiments were performed using highly purified deionized water (PureLab Option-R7; Elga, UK).

Soil Analysis

According to the ISO Standard 11464 (ISO 2006), the soil samples were air-dried, pulverized, and sieved through a 2-mm sieve prior to analysis.

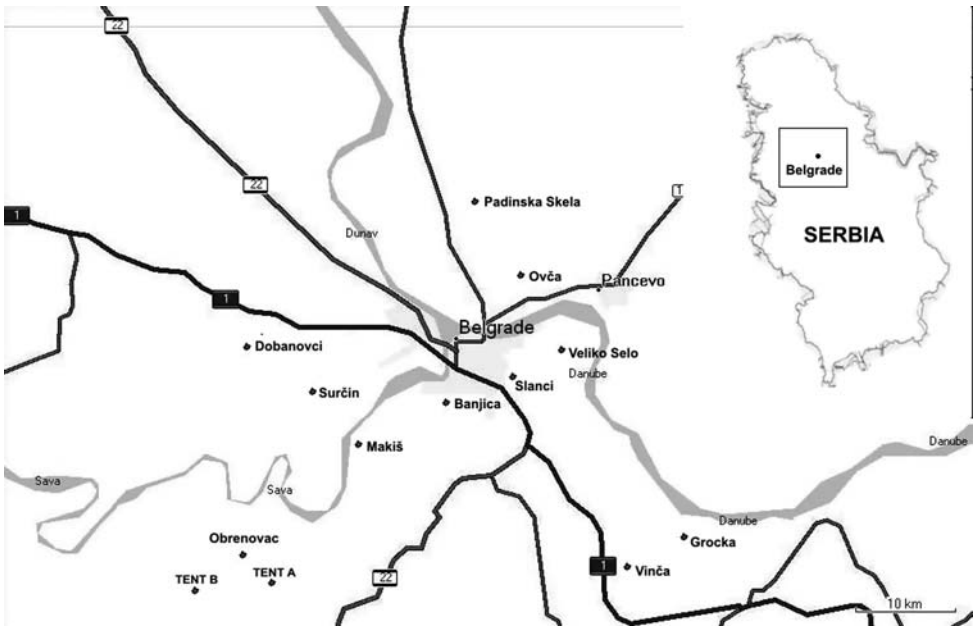

Fig. 1 Agricultural city areas studied. The most important agricultural areas of Belgrade, Serbia, where soil, vegetable, and fruit samples were collected from and analyzed to assess the levels of contamination with selected heavy metals and pesticides

For soil characterization, selected physical and chemical properties were determined using the following well-established laboratory procedures: combined sieving and pipette method with Na-pyrophosphate preparation for soil texture, the volumetric method for calcium carbonate ($CaCO_3$), and the dichromate method for total carbon. The pH values of soil in water or 1.0 M potassium chloride (KCl) solution [soil-to-water (or KCl) ratio: 1:2.5] were measured.

Increased levels of heavy metals (Zn, Cd, Cu) in soils are associated with the use of mineral fertilizers (Gaw et al. 2006 (cited in Taylor and Percival 2001)) and some Cu- or Zn-based fungicides commonly applied in horticultural production (Gaw et al. 2006; Micó et al. 2006 [cited in Tiller and Marry 1982]). Hence, at the beginning of our research we focused on Slanci, Ovča, and Obrenovac, the most important city horticultural areas, to study the agricultural soil contamination with selected heavy metals. In addition, as depicted in Fig. 1, the agricultural area of the Obrenovac territory is situated in the vicinity of coal-fired thermal power plants (TENT A and B). Because fly and bottom ash particles emitted as coal combustion products are significantly rich in toxic elements such as Pb, Cd, Zn, Cu, Cr, Mn, and so forth (Baba et al. 2003), causing severe environmental problems, the determination of selected heavy metal contents in the soil of the Obrenovac area is particularly emphasized.

Following ISO Standard 11466 (ISO 1995), extraction of heavy metals from soil samples was carried out in aqua regia. In accordance with ISO Standard 11047 (ISO 1998), determination of Pb, Cd, Cu, and Zn concentrations in aqua regia soil extracts was done by flame atomic absorption spectrometry (FAAS). A Varian SpectrAA 220 atomic absorption spectrometer with air/acetylene oxidizing flame and deuterium background correction was used. Standard stock solutions of Pb, Cd, Cu, and Zn, 1000 μg/mL concentration, were used to prepare a series of aqueous calibration standards in the following ranges: 0.10–0.60 μg/mL for Pb, 0.025–0.125 μg/mL for Cd, 1–5 μg/mL for Cu, and 0.10–0.50 μg/mL for Zn. Relative standard deviation (RSD) values for three replicate analyses were not higher than 10%. Linearity of calibration curves for metal content determination was attained for the given concentration ranges and confirmed by regression coefficients (R) better than 0.997.

Pesticides previously or recently registered in our country for soil treatment of crops raised (Mitić 2004) were selected for the soil study. Due to crop rotation, a measure frequently used in agricultural practice, some pesticides not intended for vegetable and fruit production, but stable and persistent in the environment and probably used for soil treatment previously, were also analyzed.

The study of solid-phase microextraction (SPME) applicability to pesticide residue analysis of samples having different matrices has been conducted regularly in our laboratory (Đurović and Marković 2005; Đurović et al. 2007a, 2007b, 2007c, 2007d). Accordingly, extraction of pesticide residues from soil samples was performed by a combined liquid–liquid extraction and SPME procedure. A soil portion (8 g) was homogenized for 30 min with methanol (15 mL) using a mechanical stirrer. After centrifugation and filtration, the whole procedure was repeated. The extract was evaporated to dryness and dissolved in acetone (1 mL). After dilution with water (50 times) and the addition of sodium chloride [5% solution (w/v)], a half-hour direct immersion (DI) SPME procedure, mixing included, was performed at room temperature using a 100 μm polydimethylsiloxane (PDMS) fiber (Supelco/Sigma Aldrich, Germany). Before use, the fiber was conditioned as recommended by the manufacturer. Selected extraction parameters (time and temperature) were previously optimized according to Beltran et al. (1998) by applying the whole extraction procedure to the fortified soil samples. Because the investigated soil samples exhibit different soil characteristics, considering total carbon and clay content—the parameters affecting the extraction efficiency of pesticide residues the most—a standard addition protocol was performed for accurate quantification purposes (Fernandez-Alvarez et al. 2008). Each soil sample was analyzed in triplicate.

A gas chromatograph/mass spectrometer (GC/MS) (CP-3800/Saturn 2200; Varian, Australia) was used as a detection and quantification device. Pesticides, extracted by the fiber, were thermally desorbed in a GC injector at 270°C for a previously optimized desorption time of 7 min. Analyte desorption was completed after 7 min, as confirmed by immediate blank fiber measurement. Pesticides were separated using a VF-5 ms Varian column. The GC was programmed as follows: The initial temperature was set at 120°C, then increased to 170°C at 8°C/min and held for 4.5 min, then increased to 280°C at 9°C/min and held for 5.5 min. The helium flow rate was 1.1 mL/min. The ion trap MS operated in the electron impact/selected ion monitoring (EI/SIM) mode. The ion trap and transfer line temperatures were set at 220°C and 250°C, respectively. Specific ions of the investigated pesticides were used for detection and confirmation; the quantification was conducted by an external standard method. The RSD values of three consecutive SPME-GC/MS analysis of each soil sample were lower than 19%. These values are within the range reported in the literature for both DI and headspace (HS) SPME measurements (Hildebrandt et al. 2009). The recovery values at the 0.03-mg/kg fortification level varied from 54.8% to 99.6% for all pesticides studied. Limit of detection (LOD) values were computed as three times the

baseline noise ($S/N = 3$) at the lowest detectable concentration.

Plant Product Analysis

The release of hazardous pollutants into the environment increases metal concentrations persistently, thus contaminating the food supply. Pb in food, for example, originates mainly from atmospheric deposition and adherence of Pb-rich soil particles to plants (Nasreddine and Parent-Massin 2002). Because, as already mentioned, the Obrenovac area has been affected by the coal power plants activities, the vegetable samples from this area were studied in the first research phase. Prior to metal analysis, plant product samples were prepared according to AOAC Method 922.02 (Horwitz 2002), while Pb, Cd, Cu and Zn contents were determined by FAAS, following 975.03 method (Horwitz 2002). Working standard solutions of Pb, Cd, Cu, and Zn of the same concentration ranges as for soil analysis were prepared. Linearity was attained in the concentrations ranges studied ($R \geq 0.996$). RSD values for three replicate analyses were not higher than 10%.

Most of the fruit and vegetable samples analyzed were raised on private farms and, therefore, no records of protection product applications, despite distributed questionnaires, were available. Hence, a set of pesticides registered and most commonly used in our country to protect each commodity type (Mitić 2004) was analyzed in the specific plant product. A laboratory sample size complying with the sampling method requirements for every commodity type (CEC 2002) was used to obtain a representative analytical sample. After comminution and homogenization using a home blender, 10-g replicate analytical portions of all fruit and vegetable samples, except cabbage, were equilibrated with methanol (20 mL). After centrifugation, the supernatant volume was adjusted to 100 mL with water and then 10 times diluted prior to the DI SPME procedure. Fifty-gram portions of sliced and homogenized cabbage samples were diluted with water (160 mL), mixed, and vacuum-filtrated using crucibles. The obtained filtrates were five times diluted before SPME measurement. SPME extraction parameters were optimized for each matrix and the pesticide set was investigated. Extraction was performed at room temperature using a 100-μm PDMS fiber. Extraction times varied from 30 to 60 min. Reference (pesticide-free) samples of vegetables and fruit were fortified with a standard pesticide mix and the same analytical procedure was applied. RSD values of three consecutive analysis of the same sample were not higher than 18.7%. The recovery values for vegetable and fruit reference samples fortified at the 0.1-mg/kg level of each pesticide studied were in the 54.3–119.5% range. LODs were computed as $S/N = 3$ for all matrices and pesticides studied. Pesticide multiresidue analysis was performed using the already described GC/MS device. Pesticides were desorbed at 270°C for 9 min. Separation of investigated pesticides for every commodity type was achieved applying appropriate GC temperature programs. The MS operated under the same conditions as in the soil analysis.

Results and Discussion

Soil Characterization

The selected physical and chemical properties of agricultural soils from the given areas (Fig. 1) are summarized in Table 1. As can be seen, different soil groups, according to the FAO classification (IUSS Working Group WRB 2006), are present in open fields, whereas Anhtrosol is specific for plastic sheds. In addition, the investigated soils, mostly with clay texture, are calcareous with neutral and low-alkaline reaction or noncalcareous showing neutral, medium, or very acidic reaction. The total carbon content in the soils was low to medium. According to the data obtained, the soils are very heterogeneous. Hence, various behaviors of heavy metals and pesticide residues in different soil matrices can be expected.

Heavy Metals in Soil

Disregarding the origin of heavy metals in soil, a 0–30-cm agricultural soil layer was mixed by tillage and in this way metals were distributed in the layer. Concentrations of Pb, Cd, Cu, and Zn in soils sampled in Obrenovac, Slanci, and Ovča are presented in Table 2. Heavy metal contents in all analyzed samples do not exceed either the reference values established by the Serbian national regulations (The Official Gazette of the RS 1994) or the maximum permitted heavy metal concentrations laid down in the EC directive on agricultural soils (CEC 1986). By comparing these data with the target values of the Dutch criteria for soil remediation (Anonymous 2000), it can be concluded that heavy metal concentrations (Table 2) are below or close to the Dutch limits (36, 140, 0.8, and 85 mg/kg for Cu, Zn, Cd, and Pb, respectively), indicating sustainable soil quality. Additionally, heavy metal contents close to the target values indicate the long-term environmental quality and negligible risks to the ecosystem.

The Cu contents can be compared with the levels given for agricultural soils in the Vojvodina Province, Serbia (Ubavić et al. 1993), as well as with the ranges reported for market garden land use in different regions of New Zealand (Gaw et al. 2006) and agricultural soils in the United States (Holmgren et al. 1993). The Zn concentrations are slightly higher than the values reported for rural soils in the

Table 1 Selected physical and chemical soil properties

Sample No.	Location	Cultivated plant	Soil group	Texture (%)			$CaCO_3$ (%)	pH		C (%)
				Sand (0.02–2.0 mm)	Silt (0.002–0.02 mm)	Clay (<0.002 mm)		H_2O	KCl	
1	Grocka 1	Appricot	Vertisol	27.04	31.56	41.40	0	5.81	4.99	1.44
2	Grocka 2	Appricot	Vertisol	27.20	31.44	41.36	0	5.81	4.89	1.60
3	Grocka 3	Strawberry	Cambisol	25.08	28.36	46.56	0	6.20	5.03	0.94
4	Obrenovac 1	Tomato	Vertiosol	12.72	30.72	56.24	0	7.37	6.70	4.97
5	Obrenovac 2	Tomato	Fluvisol	27.68	31.00	41.32	0	7.47	6.75	2.34
6	Obrenovac 3	Pepper	Fluvisol	23.16	33.04	43.80	0	6.22	5.32	1.69
7	Slanci 1	Tomato, onion	Anthrosol	40.80	27.72	31.48	2.25	7.53	7.06	2.33
8	Slanci 2	Tomato	Regosol	41.88	27.60	30.52	4.72	7.68	7.47	1.66
9	Veliko Selo	Tomato	Anthrosol	42.08	26.80	31.12	5.78	8.01	7.71	1.84
10	Banjica	Peach	Cambisol	30.16	27.56	42.28	0	4.99	4.05	1.18
11	Vinča	Peach	Chernozem	32.92	29.28	37.80	0.26	7.29	6.39	1.71
12	Ovča 1	Onion	Anthrosol	45.80	19.24	34.96	4.25	7.81	7.47	1.89
13	Ovča 2	Wheat	Fluvisol	51.12	23.12	25.76	5.46	7.84	7.56	1.52
14	Padinska Skela 1	Alfalfa	Fluvisol	29.36	24.36	46.28	0	6.88	6.02	1.76
15	Padinska Skela 2	Wheat	Gleysol	6.88	36.28	56.84	1.91	7.87	7.17	1.55
16	Padinska Skela 3	Pepper	Anthrosol	48.08	23.20	28.72	2.89	7.82	7.26	2.23
17	Padinska Skela 4	Apple	Fluvisol	46.00	23.52	30.48	4.58	7.75	7.14	1.27
18	Surčin 1	Wheat	Fluvisol	48.24	16.28	34.80	4.48	8.11	7.81	1.38
19	Surčin 2	Wheat	Gleysol	13.72	29.88	56.40	1.99	7.41	7.44	1.87
20	Surčin 3	Wheat	Fluvisol	23.68	24.52	51.80	1.07	7.77	7.05	1.75
21	Surčin 4	Wheat	Gleysol	25.56	30.40	44.04	2.34	7.87	7.65	2.12
22	Makiš 1	Wheat	Fluvisol	40.44	30.24	29.32	1.65	7.67	7.14	2.01
23	Makiš 2	Maize	Chernozem	33.36	38.80	27.84	0	5.80	5.03	1.79
24	Dobanovci	Maize	Chernozem	26.28	38.80	34.92	0	6.55	5.73	1.59

Table 2 Heavy metal concentrations in selected soil samples

Sample No.	Location	Concentration (mg/kg)			
		Pb	Cd	Cu	Zn
4	Obrenovac 1	27.4	0.27	34.4	95.2
5	Obrenovac 2	22.6	0.13	24.0	116
6	Obrenovac 3	21.7	0.11	20.5	75.3
7	Slanci 1	18.1	0.22	34.1	142
8	Slanci 2	13.5	0.12	23.4	79.4
12	Ovča 1	13.4	0.11	30.6	75.9

Netherlands (Van Gaans et al. 1995), some British Columbian vegetable cropping soils (Gaw et al. 2006 [cited in De Pieri et al. 1996]), and for market gardens in New Zealand (Gaw et al. 2006), but they fit well into the Zn content ranges found for soils in the Vojvodina Province, Serbia (Ubavić et al. 1993), as well as in the United States (Holmgren et al. 1993). Cd and Pb levels reported here are comparable with those given by Ubavić et al. (1993), Holmgren et al. (1993), Van Gaans et al. (1995), and Gaw et al. (2006). Finally, considering typical literature soil concentration ranges for the heavy metals studied, as well as the most common values related to their average abundance in the Earth's crust (Abollino et al. 2002 [cited in Alloway 1990]), the examined soils can be considered unpolluted as the concentrations of selected heavy metals are within the ranges typical of soils.

Pesticide Residues in Soil

The results on pesticide residues determined in soil samples are summarized in Table 3. The national regulations relevant for pesticide residues in agricultural soils (The Official Gazette of the RS 1994) define the maximum residue level (MRL) range from 0.06 to 0.40 mg/kg for atrazine [6-chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and simazine [6-chloro-*N*,*N*′-diethyl-1,3,5-triazine-2,4-diamine] only. It is obvious that the atrazine concentrations measured in soil samples from Grocka, Obrenovac, and Veliko Selo areas are below the national limit values. Referring to the Dutch target and soil

Table 3 Pesticide residues in soil samples

Pesticide	LOD* (μg/kg)	Concentration (μg/kg)																							
		Sample No.																							
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Herbicide																									
Atrazine	0.7	bd	bd	40.5	bd	bd	27.6	bd	bd	34.9	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Acetochlor	0.2	bd	bd	bd	bd	bd	bd	bd	13.3	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Dimethenamid	1.8	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Flurochloridone	0.6	bd	bd	bd	bd	bd	bd	bd	bd	46.0	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Chlorothalonil	2.4	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Chloridazon	1.2	bd	53.9	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	49.6	bd	bd	bd
Clomazone	0.1	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Linuron	3.7	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Napropamide	2.4	bd	bd	28.2	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Oxyfluorfen	0.3	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Pendimethalin	1.5	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Prometryn	0.07	bd	bd	bd	bd	bd	bd	bd	27.7	23.8	bd	bd	bd	53.6	bd	bd	bd	bd	bd	bd	bd	bd	bd	12.8	bd
Simazine	3.9	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	nd	bd
Insecticide																									
Deltamethrin	3.2	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Phorate	2.8	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Fenitrothion	0.05	bd	bd	80.5	bd	bd	bd	bd	bd	72.1	48.4	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	34.9	bd	bd	bd
Chlorpyrifos	1.2	bd	bd	36.6	bd	bd	bd	bd	bd	bd	bd	bd	bd	26.6	bd	47.4	bd	bd	bd	bd	bd	bd	bd	bd	bd
Carbofuran	3.1	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Gamma-HCH (Lindane)	0.3	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Tebupirimfos	0.02	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Terbufos	0.7	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd

bd = below detection limit

Source: Đurović RD, Gajić Umiljendić JS, Cupać SB, Ignjatović LjM (2009) Solid phase microextraction as an efficient method for characterization of the interaction of pesticides with different soil types. J Braz Chem Soc

remediation intervention values (0.0002 and 6 mg/kg, respectively) (Anonymous 2000), it can be concluded that these atrazine contents are considerably higher than the target value but well below the intervention limit indicating serious deterioration of soil functional properties. Concentrations of atrazine determined in current soil study are within a wide range reported for soils of Vojvodina Province (Kastori 1993) but lower than the values measured in cultivated soils in Hungary (Oldal et al. 2006). Because atrazine is a registered fruit protection product in our country (Mitić 2004), its detection in soil samples from Grocka 3 was expected. To the contrary, atrazine residues in soil samples from Obrenovac 3 and Veliko Selo (vegetables raised) were not expected but found, originating most likely from high application rates of previous periods. Nevertheless, the content of atrazine should be monitored continuously, as atrazine is well known to be a persistent and accumulative chemical.

Maximum permissible concentrations of other herbicides [prometryn (*N*,*N*′-bis (1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine], acetochlor [2-chloro-*N*-(etoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide], flurochloridone [3-chloro-4-(chloromethyl)-1-[3-(trifluoromethyl) phenyl]-2-pyrrolidinone], chloridazon [5-amino-4-chloro-2-phenyl-3(2*H*)-pyridazinone] and napropamide [*N*,*N*-diethyl-2-(1-naphthalenyloxy) propamide)] detected in soil samples from some studied areas have not been regulated either by the national or Dutch standard. Their residues in studied soil samples were entirely unexpected, because they are not intended for use in protection of these crops (Mitić 2004). Having in mind soil dissipation half-time (DT_{50}) values (Tomlin 2006), the herbicides (except prometryn) should not have been detected even if they had been used previously. Prometryn, a persistent triazine herbicide (Tomlin 2006) originates most likely from the previous period. However, its measured contents are comparable with the concentration range distinctive for soils in Vojvodina (Kastori 1993).

Fenitrothion [*O*,*O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate] and chlorpyrifos [*O*,*O*-diethyl *O*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate] were the only insecticides detected in the soil samples investigated. Although these pesticides are intended for soil treatment of crops raised in the current season (Mitić 2004), considering both the sampling time and DT_{50} values (Tomlin 2006), the origin of these active ingredients in soil remains an open question.

Heavy Metals in Plant Products

The contents of Pb, Cd, Cu, and Zn in selected vegetable samples are reported in Table 4. It is obvious that the Pb content in most of vegetable samples originating from different locations of Obrenovac is higher in comparison with the maximum levels defined by the Codex Alimentarius Standard (FAO/WHO 1995). The concentrations of Cd in all samples collected from the Obrenovac 2 location are over the values regulated by both national regulation (The Official Gazette of the FRY 1992) and Codex standard, whereas Cd concentrations in onion and cabbage samples from the Obrenovac 1 location are below permissible levels. The most extreme values, even four and three times higher than the national permissible level, were found for pepper and tomato samples, respectively, grown in open field of the Obrenovac 2 location. To estimate the risk associated with dietary intake of Cd and Pb contents, exceeding permissible levels, weekly intakes [μg/kg body weight (bw) for 60-kg person] were calculated for potato and tomato and compared with provisional tolerable weekly intake (PTWI) established as 7 and 25 μg/kg bw for Cd and Pb, respectively (WHO 1993). Cd and Pb intakes for cabbage and pepper were not calculated since consumption quantities of these vegetables in our country were not available (FAO 2003). Higher percantage of PTWI (% PTWI) obtained for Cd (14.9–99.7%), contrary to significantly lower Pb intake values (from 2.7% to 7.5% PTWI), indicates that the consumption of potatos and tomatos could pose a risk to consumers' health. Nevertheless, the results obtained unambiguously justify the investigations performed, emphasizing the need for a detailed and continuous control of heavy metal contamination in the Obrenovac area. As both sampling locations are situated in the vicinity of coal-fired thermal

Table 4 Heavy metal concentrations in selected plant product samples

Plant product	Concentration (mg/kg)			
	Pb	Cd	Cu	Zn
Obrenovac 1				
Potato (open field)	0.199*	0.086**	0.534	5.11
Tomato (open field)	0.230*	0.674#	9.11	15.3
Onion (open field)	0.106*	0.047	2.09	8.07
Cabbage (open field)	0.278	0.012	2.19	1.46
Pepper (open field)	0.252*	0.243#	8.21	15.1
Obrenovac 2				
Tomato (plastic shed)	0.112*	0.431#	7.43	17.8
Tomato (open field)	0.309*	1.15#	12.4	21.3
Tomato (plastic shed)	0.124*	0.186#	4.69	13.5
Pepper (plastic shed)	0.412*	0.240#	6.55	17.0
Pepper (open field)	0.024	0.468#	7.30	19.3
Cabbage (open field)	0.330*	0.101#	2.99	17.4

* Above Codex MRLs

** Above national MRLs

Above national and Codex MRLs

power plants as permanent contamination sources, reduction of toxic elements emission in the environment should be considered as well.

The concentrations of Cu and Zn in the samples are lower in comparison with the national and Codex limit values. In addition, these concentrations are well below average critical and toxic concentrations of Cu and Zn in cultivated plants (Kastori et al. 1997).

Pesticide Residues in Plant Products

Pesticide residues in tomato, cabbage, pepper, onion, potato, and cucumber samples are tabulated in Tables 5, 6, 7, 8, 9, 10, respectively. Because different pesticides are registered for each plant product protection, different compounds were studied in every commodity type. Concentrations of all active ingredients studied in peach and apricot samples were below the relevant LOD values.

The first step to estimate the risk associated with dietary intake of pesticides by the consumer is to compare the detected amount with the MRLs authorized in foodstuffs (Nasreddine and Parent-Massin 2002). The obtained results are compared with the MRLs established for each commodity type by national (The Official Gazette of the FRY 1992) and international (CEC 1990; FAO/WHO 2008) regulations. Concentrations of most investigated pesticides in cabbage and cucumber samples (Tables 6 and 10) are below the LOD values, whereas the content of the active ingredients detected do not exceed the MRLs. To the contrary, the concentrations of metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4*H*)-one] and trifluralin [2,6-dinitro-*N*,*N*-dipronyl-4(trifluoromethyl) benzeamine] in tomato samples collected from Ovča 1 location (Table 5) as well as the content of pendimethalin [*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine] in pepper samples from the Obrenovac 2 location (Table 7) are significantly higher than the national MRLs. Regarding both the time of application (Mitić 2004) and sampling, the probability of detecting these herbicide residues in tomato and pepper samples was strong. However, high concentrations of these herbicides indicate their inappropriate application (application rates and preharvested intervals) as the most probable source of contamination.

Concentrations of bifenthrin [2-methyl[1,1′-biphenyl]-3-yl) methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethyl-cyclopropanecarboxylate], chlorpyrifos, and cypermethrin

Table 6 Pesticide residues in cabbage samples (open field)

Pesticide	LOD (mg/kg)	Concentration (mg/kg)		
		Location		
		Ovča 1	Obrenovac 1	Obrenovac 2
Oxyfluorfen	0.099	bd	bd	bd
Pendimethalin	0.026	bd	bd	bd
Bifenthrin	0.101	bd	bd	0.18
Diazinon	0.010	bd	bd	0.09
Endosulfan (I)	0.031	bd	bd	bd
Endosulfan (II)	0.026	bd	bd	bd
Chlorpyrifos	0.091	bd	0.11	bd
Malathion	0.022	0.09	bd	bd

bd = below detection limit

Table 5 Pesticide residues in tomato samples

Pesticide	LOD (mg/kg)	Concentration (mg/kg)						
		Location						
		Ovča 1 (plastic shed)	Padinska Skela 3 (plastic shed)	Obrenovac 2 (plasic shed)	Obrenovac 2 (open field)	Obrenovac 2 (plastic shed)	Obrenovac 1 (open field)	Slanci 1 (plastic shed)
Metribuzin	0.015	0.76*	bd	bd	bd	bd	bd	bd
Napropamide	0.017	bd	bd	bd	bd	bd	bd	bd
Trifluralin	0.004	0.12*	bd	0.01	0.05	0.05	bd	bd
Bifenthrin	0.005	bd	bd	bd	bd	bd	bd	bd
Cypermethrin	0.007	0.16	bd	0.07	bd	0.04	bd	bd
Deltamethrin	0.007	0.09	bd	bd	bd	bd	bd	0.07
Fenitrothion	0.018	bd	bd	bd	bd	bd	bd	bd
Malathion	0.015	bd	0.16	bd	bd	bd	bd	bd
Pirimyphos-methyl	0.015	bd	bd	bd	bd	bd	bd	bd
Dimethomorf	0.015	bd	bd	bd	bd	bd	bd	bd
Famoxadone	0.005	0.15	0.30	bd	bd	0.1	bd	bd
Vinclozolin	0.007	bd	bd	bd	0.01	bd	bd	bd

bd = below detection limit

* Above national MRLs

Table 7 Pesticide residues in pepper samples

Pesticide	LOD (mg/kg)	Concentration (mg/kg)		
		Location		
		Obrenovac 1 (open field)	Obrenovac 2 (open field)	Obrenovac 2 (plastic shed)
Napropamide	0.016	bd	bd	bd
Pendimethalin	0.001	bd	bd	0.52*
Trifluralin	0.0003	bd	bd	bd
Diazinon	0.0005	bd	bd	bd
Malathion	0.0004	0.009	bd	bd
Pirimiphos-methyl	0.0004	bd	bd	bd

bd = below detection limit

* Above national MRLs

[cyano (3-phenoxyphenyl) methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate] found in potato samples from Slanci 1 and Obrenovac 1 locations (Table 9) are several times higher compared with national and international MRL values. If these insecticides had been applied according to the instructions (Mitić 2004), such high residue levels would not have been found, particularly in the case of early potatoes. The content of fluazifop-*P*-butyl (butyl (*R*)-2-[4-[[5-(trifluoromethyl)-2-pyridinyl]oxy] phenoxy] propanoate) herbicide slightly below the relevant national limit value was expected because it had been used for weed control of potatoes during the whole vegetation period. Several times higher pendimethalin contents in samples from the Slanci 1 and Obrenovac 1 location than the national MRL indicate that pendimethalin-based products for potato protection were not used as recommended.

The concentration of chlorpyrifos in the onion sample from Slanci 1 location (Table 8) is more than 20 times higher than the national and international MRL, confirming unambiguously its inappropriate use. This conclusion is even more important as the use of chlorpyrifos for the protection of vegetables grown at the beginning of the season is not allowed. Additionally, high pendimethalin concentrations measured in onion samples from both locations confirm already mentioned inappropriate application of this herbicide.

Table 8 Pesticide residues in onion samples (open field)

Pesticide	LOD (mg/kg)	Concentration (mg/kg)	
		Location	
		Slanci 1	Obrenovac 1
Fluazifop-*P*-butyl	0.002	0.19	bd
Oxyfluorfen	0.0003	bd	bd
Pendimethalin	0.0007	0.70*	0.23*
Fenitrothion	0.0004	bd	bd
Chlorpyrifos	0.004	1.18#	bd
Malathion	0.001	bd	bd
Vinclozolin	0.001	0.19	bd

bd = below detection limit

* Above national MRLs

Above national and international MRL values

Table 9 Pesticide residues in potato samples (open field)

Pesticide	LOD (mg/kg)	Concentration (mg/kg)	
		Location	
		Slanci 1	Obrenovac 1
Acetochlor	0.002	bd	bd
Dimethenamid	0.002	bd	bd
Fluazifop-*P*-butyl	0.007	0.54*	0.53*
Flurochloridone	0.005	0.05	bd
Metribuzin	0.018	bd	bd
Pendimethalin	0.001	0.74*	0.28*
Bifenthrin	0.011	0.49#	0.24#
Cypermethrin	0.017	0.50#	bd
Deltamethrin	0.018	bd	bd
Dimethoate	0.014	bd	bd
Endosulfan (I)	0.008	bd	bd
Endosulfan (II)	0.010	bd	bd
Fenitrothion	0.004	0.005	bd
Fipronil	0.009	0.03	bd
Foksim	0.011	bd	bd
Chlorpyrifos	0.002	0.10#	0.11#
Carbosulfan	0.016	bd	bd
Malathion	0.007	bd	bd
Methidation	0.001	bd	bd
Dimethomorph	0.002	bd	bd
Famoxadone	0.001	bd	0.44
Metalaxyl	0.018	bd	bd

bd = below detection limit

* Above national MRLs

Above national and international MRLs

As the pesticide residue levels in most of the plant products investigated exceeded the MRLs, strongly indicating violation of good agricultural practice, there is no doubt that consumer health might be endangered. To assess health risk based on pesticide exposure, estimated dietary intakes (EDIs) of bifenthrin, cypermethryn, and chlorpyrifos residues, found in potato samples from Slanci 1 and Obrenovac 1 locations, were calculated and compared with the acceptable daily intakes (ADIs) (Nasreddine and Parent-Massin 2002). Food consumption quantities for other commodities, as well as ADI values for other pesticides, were not available (FAO 2003; Codex Alimentarius Commission 1998). The obtained hazard index values

Table 10 Pesticide residues in cucumber samples (plastic shed)

Pesticide	LOD (mg/kg)	Concentration (mg/kg)
		Location
		Padinska Skela 3
Bifenthrin	0.017	0.08
Cypermethrin	0.004	bd
Deltamethrin	0.007	bd
Fenitrothion	0.0003	bd
Malathion	0.002	bd
Pirimiphos-methyl	0.017	bd
Dimethomorph	0.011	bd
Metalaxyl	0.012	0.24
Myclobutanil	0.011	bd
Vinclozolin	0.0004	bd

bd = below detection limit

(EDI/ADI), ranging from 0.019 to 0.045, did not point to a serious risk to consumers' health. Nevertheless, the results of the present study indicate the necessity for a controlled application of these plant protection products as well as a continual monitoring of pesticide residues in plant products for human consumption.

Conclusion

The data collected in this study provide an insight into the level of Belgrade agricultural area contamination with pesticide residues and heavy metals. Bearing in mind low Pb, Cd, Cu, and Zn concentrations, examined soils (heterogeneous with respect to their physical and chemical properties) are considered unpolluted and of sustainable quality. On the other hand, Pb and Cd contents higher than the maximum national and Codex levels were detected in most of the vegetable samples from the Obrenovac area, indicating emission of coal combustion products from thermal power plants as a possible source of contamination. Residues of herbicides (atrazine, prometryn, acetochlor, flurochloridone, chloridazon, and napropamide) and insecticides (fenitrothion and chlorpyrifos) were detected in some soil samples. According to their DT_{50} values as well as parameters relevant for application and sampling, detection of these pesticide residues was unexpected. However, what is more important, the concentrations of herbicides (metribuzin, trifluralin, and pendimethalin) and insecticides (bifenthrin, chlorpyrifos, and cypermethrin) in vegetable samples from Slanci, Ovča, and Obrenovac areas exceeding the relevant MRLs point out the existence of a potential risk to human health.

Due to higher levels of heavy metals and pesticide residues in plant products, grown in the most important agricultural areas, as well as the presence of pesticide residues in some soil samples, their continual monitoring is strongly recommended as a first preventive measure to minimize human health risks. Therefore, to complete an established contamination database, more detailed sampling and analysis of agricultural soils and plant products should be done in the next research phase. In addition, because higher pesticides levels detected are probably the consequence of inappropriate use of plant protection products, an important forthcoming activity will be to instruct farmers to use them according to application rules as well as to keep a record of all protection product applications.

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