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Mercury content in agricultural soils (Vojvodina Province, Serbia)

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Abstract The Vojvodina Province in northern Serbia is well known for its intensive field crops production. Over 90 % of total arable land, which represents more than 1500.000 ha, is used for field or vegetable crop production. A grid superimposed on Vojvodina land by means of a GIS tool (GIS ArcView 10) has divided land into 4 × 4 km units, each representing an area of 1600 ha. Total number of 1370 bulked soil samples were taken (0–30 cm depth) from agricultural land and analysed for total mercury content THg. The samples were analysed using Direct Mercury Analyzer DMA 80 Milestone. Quality control was carried out with IRMM BCR reference materials 143R. The aim of this study was to determine the total content of Hg in agricultural soils and its spatial distributions in different parts of Vojvodina Province. The obtained results were within interval 0.008–0.974 mg kg^{-1}. The average concentration of Hg was 0.068, with median 0.048 mg kg^{-1}. The correlation was determined between Hg concentration and organic matter content in the soil. Content of Hg coincides with main geomorphological units of Vojvodina Province. Average values of Hg concentrations for soils formatted on different geomorphological units were 0.031 for sandy area with dune fields, 0.048 for alluvial terraces, 0.055 for upper Pleistocene terraces, 0.058 for loess plateaus, 0.083 for mountains and 0.092 mg kg^{-1} for alluvial plains. Hg spatial distribution confirmed that most of Vojvodina Province area has geochemical origin of Hg. Higher concentration of Hg on alluvial plains indicated that the origin of Hg near rivers could be from anthropogenic source. The main rivers in Vojvodina have been dammed more than a century ago. Thus, higher concentrations of Hg in their alluvial plains out of narrow dammed zone around the rivers must be related to natural and anthropogenic sources located in their huge catchments. Higher content of Hg in mountain region can be explained by high clay content in these soils. Additional hotspots of Hg concentration of top soils are related to geographical locations of major towns. The obtained results also indicated that the measured levels of Hg in the soil are not limiting factors for production of safe food in Vojvodina.

Keywords Soil · Mercury · Hg · Vojvodina Province · Heavy metals

Responsible Editor: Philippe Garrigues

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Introduction

Soil is a natural resource which is non-renewable in real time because it takes a long time to form and it is quickly destroyed. Soil is subject to increasing pressure exacted by the global progress and it cannot be considered separately from other environmental factors, but only within the framework of an all-inclusive system of environmental protection (Sekulic et al. 2011).

Mercury pollution is a significant global concern, not only due to its increased level in the environment but also due to its toxic effect on human health (He et al. 2015). Hg takes three

major forms in the environment, namely methyl-Hg (MeHg), Hg^0 and Hg^{2+}. All three forms of Hg adversely affect the natural environment and pose a risk to human health (Li and Tse 2015). The most important geochemical features of Hg are (i) affinity to form strong bonds with S, e.g. cinnabar HgS is the most common Hg mineral; (ii) formation of organomercury compounds that are relatively stable in aqueous media; (iii) volatility of elemental Hg. Hg in soil occurs in several ionic species and it is susceptible to transformations through the following processes: reduction, oxidation, formation of organic compounds and hydration. Hg is retained by soils mainly as slightly mobile organocomplexes (Kabata-Pendias and Pendias 2001).

The mercury that enters the environment is generally acknowledged to have two sources: natural and anthropogenic (Li and Tse 2015). Natural sources of mercury released to the atmosphere include volcanoes, evaporation from soil and water surfaces, degradation of minerals and forest fires (Ottesen et al. 2013). The burning of fossil fuels, metal mining and industrial activities, such as ore processing and cement production, particularly coal and oil combustion and gold production, are the major anthropogenic sources of Hg release (Li and Tse 2015). More directly, soil contamination can also result from the disposal of liquid or solid Hg sources (accidental spilling, mine tailings, landfills, polluted sewage sludge, etc.) (Leterme and Jacques 2015). Soil contamination with mercury during mining activities was a subject of many papers all over the world (Dadova et al. 2015; Dai et al. 2013; Ordonez et al. 2013).

Atmospheric deposition is the primary cause of Hg contamination (He et al. 2015; Shi et al. 2013). According to Serbian Environmental Protection Agency, Hg emission for 2013 in Serbia was 1.44 Mg; values of emissions were obtained in accordance with the methodology EMEP/EEA to the UNECE Convention on Transboundary Air Pollution (CLRTAP) (STAT. YEARB. SERB. 2015). Since the atmospheric deposition is the main source of soil contamination with mercury that has a cumulative effect (Tang et al. 2015), it is very important to know the background limit of Hg soil and to monitor the soil quality. Establishing Hg background levels in various soils is problematic. The main problem is distinguishing human input (pollution) from natural Hg input (Rodriguez Martin et al. 2013). Geostatistical methods and geographic information system (GIS) mapping have been used in numerous studies to determine spatial distribution and behavior of heavy metals in soils and to identify their sources (Burak et al. 2010; Maanan et al. 2013; Mihailovic et al. 2014; Rodriguez Martin et al. 2009; Shan et al. 2013; Shi et al. 2013).

Reimann and Garrett (2005) indicated the significance of local establishment of background levels, since it changes from one area to another and with the scale of the studied area. In addition, when mapping at the large continental scale, natural element concentrations can be as high as anthropogenic

contamination, or even above it. These will usually be restricted to the local scale. This is the first detailed and systematic study of Hg content in Vojvodina, which will contribute to the further monitoring of Hg content in this region.

Hg could be introduced and accumulated in soil through various pathways. On the other hand, Hg in soil could be evaporated to the atmosphere, thus soil becomes an important source of Hg (Shi et al. 2013). Methylmercury is bioavailable and can be bioaccumulated within food webs. Many studies have confirmed the biomagnification Hg in the food chain (Krasinska and Falandysz 2015; Saba et al. 2015; Zhou et al. 2015).

The Vojvodina Province has been recognized as having a high potential for field crop production on account of its fertile soils, moderate climate, abundant water resources and a long tradition in crop production. Therefore, soil protection is of crucial importance for economic development of the Vojvodina Province. The aim of this study was to determine the total content of Hg (THg) in agricultural soils from the aspect of soil suitability for a production of healthy and safe food and its spatial distributions in different parts of Vojvodina Province.

Materials and methods

Study area

Vojvodina is the autonomous province in Republic of Serbia and occupies an area between 44° 38′ and 46° 10′ northern latitude and 18° 10′ and 21° 15′ eastern longitude. It is the northernmost part of Serbia, bordered by Croatia to the west, Hungary to the north and Romania to the east (Fig. 1). Vojvodina is situated in the southeastern part of the Pannonian (Carpathian) Basin, the plain that remained when the Pliocene Pannonian Sea dried out. As a consequence of this, Vojvodina is rich in fertile loamy loess soil. Regarding the distribution of soil types, as much as 60 % of the area of the Vojvodina Province are chernozems, which are considered ideal for crop production according to their physical and chemical properties. The other fertile soil types that occupy considerable areas are the hydromorphic black soils at 16 % and the alluvial soils at 9 % (Skoric et al. 1985). Out of the total area of the Vojvodina Province (2,150,600 ha), the agricultural land takes 1,694,000 ha or 80 %. According to the mode of land exploitation, the Vojvodina Province is a typical rural region in which ploughed land and gardens cover 90 % of the agricultural land (STAT. YEARB. SERB. 2015). Agriculture is a priority economic sector in Vojvodina. The share of agribusiness in the total industrial production is 40 %, which is 30 % in the total exports of Vojvodina. Fine chernozem soils make Vojvodina the main agricultural resource of Serbia; the region supplies much of the country's wheat, maize and soybean (STAT. YEARB. SERB. 2015). Many
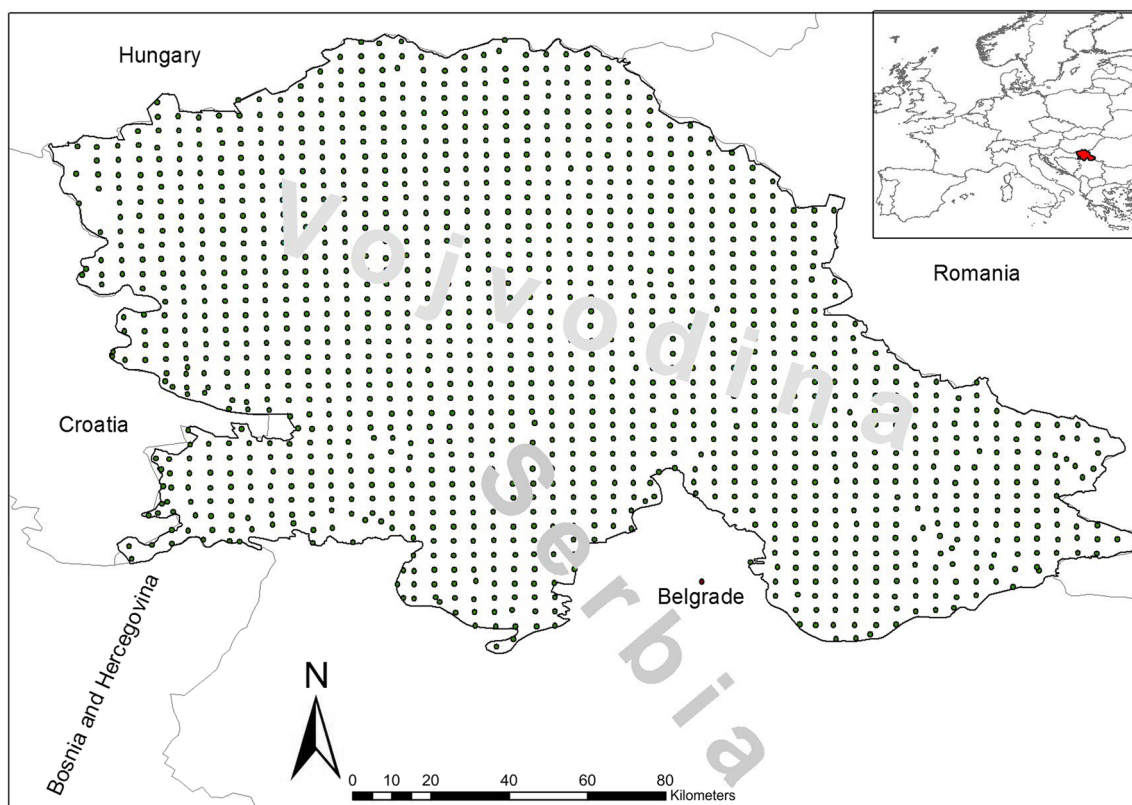
Fig. 1 Layout of 1370 taken soil samples

cash crops are also grown there, notably sugar beets and oilseeds, which are processed by regional enterprises.

Vojvodina is located in the southeastern part of the Carpathian (Pannonian) Basin, encompassing the confluence area of the Danube, Sava, Tisa (Tisza) and Tamiš (Temeş) rivers (Fig. 1) (Popov et al. 2012). More than 60 % of this lowland area is covered by loess and loess-like sediments at terraces and loess plateaus (Markovic et al. 2008). Beside four lowland geomorphological units—sandy area, loess plateaus, upper Pleistocene and alluvial terraces and alluvial plains, the most distinctive landforms of the Vojvodina region are two mountains: Fruška Gora Mountain, which is situated between the Danube and Sava rivers, and Vršačke Mountains, which are located in the southeastern part of the region close to border with Romania (Fig. 4). The climate of Vojvodina is moderate continental, with cold winters and hot and humid summers, large range of extreme temperatures and unequal distribution of rainfall per months, which led to different values of aridity types. The mean annual air temperature is 11.1 °C and the annual amount of precipitation is about 600 mm (Hrnjak et al. 2014; Tosic et al. 2014). Potential vegetation is mostly replaced by crops at lowland zone. Forest vegetation is limited to narrow belts close to the rivers, Deliblato sandy area and two mountains. Vojvodina has a population of about one million inhabitants (about 27 % of Serbia's total).

Sample collection and processing

A grid superimposed on Vojvodina land by means of a GIS tool GIS ArcView 10 has divided the land of the Vojvodina into 4 × 4 km units, each representing an area of 1600 ha (Fig. 1). Samples were taken from defined spots of agricultural land or the centre of each quadrant using GPS manual receivers (GPS receivers Trimble GPS GeoXH 3000, Trimble GPS Juno SC, Terrasync Professional software). In case of impossibility to sample from the centre of a quadrant, for any reason, the correction was performed at the nearest corresponding location distant from the defined spot up to 500 m and rarely up to 1000 m (Fig. 1). If the defined spots were in the urban area, the samples were taken from urban gardens and garden plots. A total of 1370 bulked soil samples were taken during the period 2011–2013. The topsoil samples were taken from depth 0–30 cm. This depth was chosen as a zone of the most active root systems of field crops. The samples were taken using a soil drill agrochemical probes and stored in polyethylene bags. Samples were stored in cold (+4 °C) during transport. One composite sample represented 10–15 sub-samples from random points within about 300 m² grid in each sampling site. The initial quantity of samples was approximately 1.5 kg. The soil samples were air-dried (room temperature), milled and sieved to a particle size of <2 mm, in accordance with ISO 11464 (2006).

Laboratory analysis

All laboratory analyses were performed at the Laboratory for Soil and Agroecology of the Institute of Field and Vegetable Crops, accredited according to the standard ISO/IEC 17025 (2005). The pH value in 1:5 (*v/v*) suspension of soil in 1 mol/L KCl was determined using a glass electrode according to ISO 10390 (2010). The carbonate content, as $CaCO_3$ content, was determined according to ISO 10693 (1995) volumetric method. The organic matter content was measured by oxidation using the sulfochromic oxidation method by ISO 14235 (1998).

The samples were analyzed for total mercury content using Direct Mercury Analyzer DMA 80 Milestone, which combines techniques of thermal decomposition, catalytic conversion, amalgamation and atomic absorption spectrophotometry ($\lambda = 253.65$ nm) in solid soil samples. The limit of detection for total mercury content was 0.0033 mg kg^{-1}. Quality control was periodically carried out with IRMM BCR reference materials 143R and deviations were within ±5 % of the certified values.

Geochemical mapping

The GIS mapping technique was employed to produce the spatial distribution maps of total mercury concentrations observed in the land of the Vojvodina Province. The software used for the mapping and spatial analysis was ESRI ArcGIS Geostatistical Analyst 10. The total mercury concentration is interpolated with the geostatistical analyst using a spatial interpolation method of inverse distance weighting (IDW) from ArcGIS 10. Grid was performed based on a size of 4 × 4 km units using available input points.

Statistical analysis

Parameters of descriptive statistics (minimum, maximum and mean value; median value; standard deviation; coefficient of variation and percentiles) were shown for total mercury content (mg kg^{-1}) in agricultural soils of Vojvodina Province. All statistical parameters were shown in tables and box-plot graphs. The significance of the differences in the total mercury content between the geomorphological units of agricultural soils was determined using the Duncan multiple range test ($p \leq 0.05$). In order to confirm the relationship among content of total mercury and different chemical traits, a Pearson's correlation analysis was applied to dataset. All statistical analyses were performed using the data analysis software system Statistica for Windows, version 12 (Dell Inc. 2015).

Results and discussion

Mercury concentration in soil

The obtained results of Hg concentrations in agricultural soils of Vojvodina are shown in Table 1 and Fig. 2. The obtained results were within the interval 0.008–0.974 mg kg^{-1}. This interval is complied with the most cited range 0.01–1 mg kg^{-1} in soils without known nearby contamination sources (Shi et al. 2013). The average concentration of Hg was 0.068 mg kg^{-1}, with median of 0.048 mg kg^{-1}. High variation coefficient value CV (119.9 %) points out high heterogeneity of tested soil samples (Table 1); similar values of CV were obtained by Rodriguez Martin et al. (2009).

Average value of THg in Vojvodina soil of 0.068 mg kg^{-1} is very close to typical concentration of Hg for world soils, which is reported at about 0.06 mg kg^{-1} (Adriano 2001). In addition, it coincides with the national average for China soils of 0.065 and Liaoning Province of 0.064 mg kg^{-1} (Shi et al. 2013).

Based on GEMAS project, median value of 0.035 mg kg^{-1} (range <0.003–1.56) was established for European countries (33 countries, 5.6 million km^2) (Ottesen et al. 2013) in agricultural soils. In this study, median value amounts to 0.048, which means that median value in agricultural soils of Vojvodina is slightly higher than the European average. However, median value for Central European countries (where Serbia belongs) amounts to 0.050 mg kg^{-1} (Ottesen et al. 2013), which is a value obtained in this study also.

Calculated on the world scale, kastanozems and chernozems in surface soils ranged from 0.02 to 0.53 with mean 0.1 mg kg^{-1} (Kabata-Pendias and Pendias 2001). Hg content in Vojvodina soils is slightly lower compared to Hg content worldwide, since 60 % of Vojvodina area is covered with chernozem. According to this global assessment, soils that are rich in organic matter have higher Hg content.

As a result of mercury extraction and use, establishing background levels in various soils is problematic. The variation between different soil types is much larger than in rock types, which is to be expected considering the greater number of environmental and chemical interactions occurring at this level of the ground. Upper limits to background Hg concentrations in most world soils are suggested to be in the range 0.15–0.2 mg kg^{-1} (Hooda 2010). Hg content values in Vojvodina soils are significantly below this upper background limit.

According to previous studies based on 70,189 samples of arable land (Sekulic et al. 2011), the Vojvodina soils are neutral (pH 6.2–7.2) to slightly alkaline (pH 7.2–8.2). Due to the aridity of the climate and the geological substrates rich in bases sedimentary rocks—loess, the soils of Vojvodina dominantly belong to the class of slightly alkaline soils (61 % of areas) and neutral soils (24 % of areas). According to the content of calcium carbonate, poorly to highly calcareous soils

Table 1 Statistical summary of total mercury content (mg kg^{-1}) in agricultural soils of Vojvodina Province

Statistical parameters	Value
Number of samples	1370
Minimum value	0.008
Percentiles 25 %	0.039
Median	0.048
Percentiles 75 %	0.065
Maximum values	0.974
Average	0.068
Standard deviation	0.081
Coefficient of variation (%)	119.9
IQR[a]/median	0.530

[a] Inter-quartile range, difference between 75th and 25th percentiles

are equally represented in the Vojvodina Province. According to the content of organic matter, 60 % of Vojvodina area belong to humic soils (3–5 % OM) and 39 % of area belong to slightly humic soils (1–3 % OM).

According to the established correlations shown in Table 2, pH reaction is highly significantly correlated to CaCO$_3$ content, which is expected. It was determined that Hg content is in statistically significant negative correlation to pH value ($r = -0.062*$), while statistically significant correlation was not found between Hg and CaCO$_3$ content. In the study of Erbo basin soils (Rodriguez Martin et al. 2009), negative correlation of THg with both pH and CaCO$_3$ content was found, while in soil of Spanish Island significant correlation with CaCO$_3$ content was not found (Rodriguez Martin et al. 2013). According to Shi et al. study Shi et al. (2013) performed in China, pH significantly correlated with THg in only one region.

Hg content was significantly correlated to the content of organic matter ($r = 0.191**$), which confirms previous studies (Rodriguez Martin et al. 2009, 2013; Shi et al. 2013). Shi et al. (2013) pointed out that the influence of TOC on Hg concentrations is more significant than that of pH. According to the established reactive transport model for mercury fate in contaminated soil, Leterme et al. (2014) and Leterme and Jacques (2015) emphasized the importance of DOM concentration in soil water as critical parameter due to the strong interaction between Hg^{2+} and the thiol groups. Same authors mentioned Hg sorption on SOM in particular with the fulvic and humic acids as other important parameters. The strong link of Hg concentration with organic material contents is also confirmed in studies of Ottesen et al. (2013), especially in the relatively high Hg levels in the Scandinavian soils.

The accumulation of Hg is related to the organic C and S levels in soils and is distributed in the surface soils at several times the concentration in the subsoils. Generally, organic soils have a higher Hg content than mineral soils. This is mainly due to a great capacity of humus, especially raw humus, for binding Hg (Kabata-Pendias and Pendias 2001). In soils of coniferous forests, eastern of the Tibet Plateau, China THg concentrations in the soil, C-layer soil showed the same value between 1990 and 2013, while the THg concentration in A-layer soil (0.085 mg kg^{-1}) in 2013 was significantly higher than the figure (0.025 mg kg^{-1}) in 1990 (Tang et al. 2015). Since Hg has cumulative effect in the soil, it is very important to determine background concentrations of Hg and to monitor Hg concentrations.

Content of Hg in all tested samples was below the threshold of 2 mg kg^{-1}, which is the maximum allowable concentration MAC for agricultural soils as prescribed by the laws of the
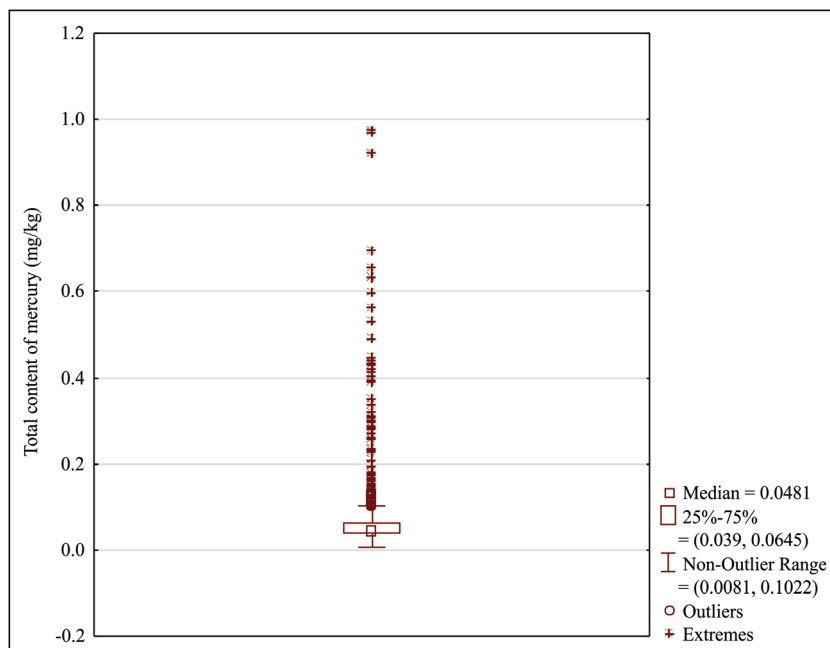
Fig. 2 Box-plot graphical display of total mercury content (mg kg^{-1}) in agricultural soils of Vojvodina Province

Table 2 Correlation coefficients between total content of mercury THg ($mg \, kg^{-1}$), pH values in 1 M KCl, content of $CaCO_3$ (%) and organic matter contents (%), for observed samples of agricultural soils of Vojvodina Province

	pH	$CaCO_3$	Organic matter	THg
pH	1.000	0.580**	−0.050	−0.062*
$CaCO_3$		1.000	−0.035	0.015
Organic matter			1.000	0.191**
THg				1.000

*p = 0.95, significantly correlated

**p = 0.99, significantly correlated

Republic of Serbia (OG RS 23/94 1994). The obtained results also indicated that the measured levels of Hg in the soil are not limiting factors for production of safe food in Vojvodina.

Spatial distribution of Hg

Spatial distribution of Hg concentrations in soils of Vojvodina was based on obtained values of data frequency (Fig. 3). The majority of present results were within the intervals 0.025–0.05 and 0.05–0.075 $mg \, kg^{-1}$, 704 and 369 of total 1370 samples, respectively. Based on GEMAS Project, a small part of northern Vojvodina was in class 0.018–0.029, according to Hg content, while the rest of Vojvodina was in class 0.029–0.048 $mg \, kg^{-1}$ (Ottesen et al. 2013), which confirms present studies.

Based on Hg spatial distribution, it was determined that the content of Hg coincides with main geomorphological units of

Vojvodina Province. Based on GEMAS project, it was concluded in the studies that geology is the main factor determining the observed Hg concentrations in the soils; also climate and soil type play an important role in influencing the observed Hg levels (Ottesen et al. 2013). In the study of Odumo et al. (2014), the effect of landforms on Hg content in soil was confirmed; in medium-gradient hill, mean value was 0.09, while in plain, it was 0.14 $mg \, kg^{-1}$. However, in studies of Rodriguez Martin et al. (2014), the Hg content in agricultural soils exhibited a low spatial correlation, since the Hg soil concentration was not linked to the main geological features of the study area.

Comparison between Figs. 3 and 4 shows significant correspondence between spatial distribution of the main relief units and Hg in soils of Vojvodina. Higher concentrations of Hg in top soils are indicated in alluvial plains of the Danube, the Sava, the Tisa and the Tamiš rivers and in the central part of the Fruška gora Mt. and southern slopes of the Vršačke mountains.

In this study, the low-concentration Hg occupies sandy terrain. The concentration of mercury within interval 0.025–0.05 and 0.05–0.075 $mg \, kg^{-1}$ occupies loess plateau and upper Pleistocene terraces. Spatial distribution of the obtained results confirmed that Hg concentration is higher in soils that are richer in organic matter. The concentration of mercury above 0.075 $mg \, kg^{-1}$ occupies mountains and alluvial plain areas of four main rivers in Vojvodina Province.

Based on processed values of Hg content for every geomorphological unit (Table 3, Fig. 5), there are sandy areas, alluvial terraces and upper Pleistocene terraces, from one side, and mountains and alluvial plains, from the other. Hg content
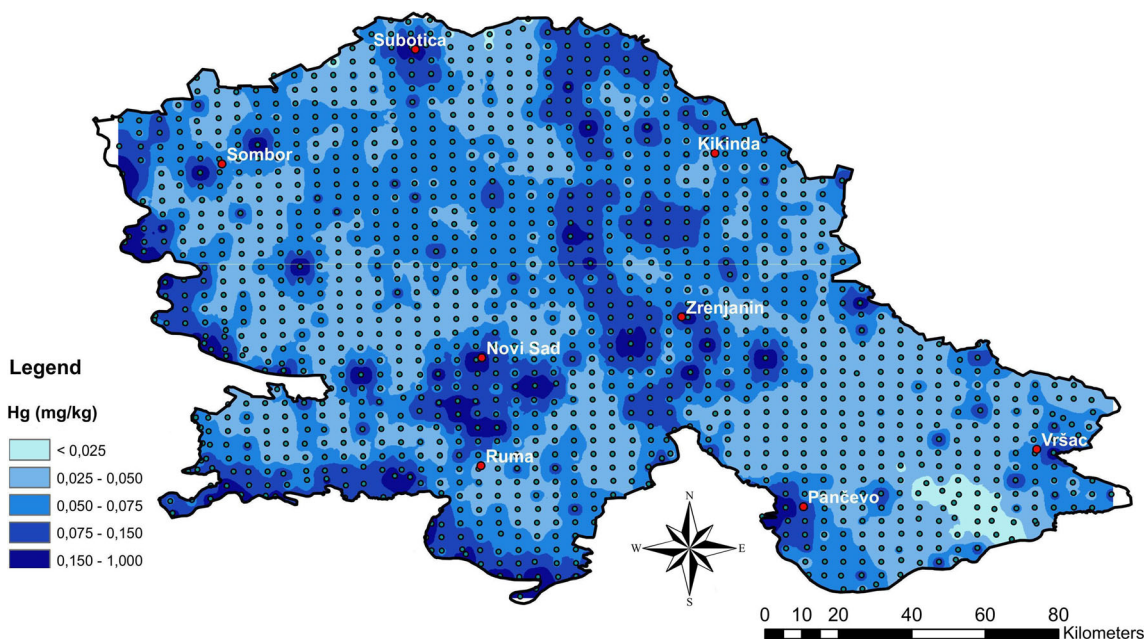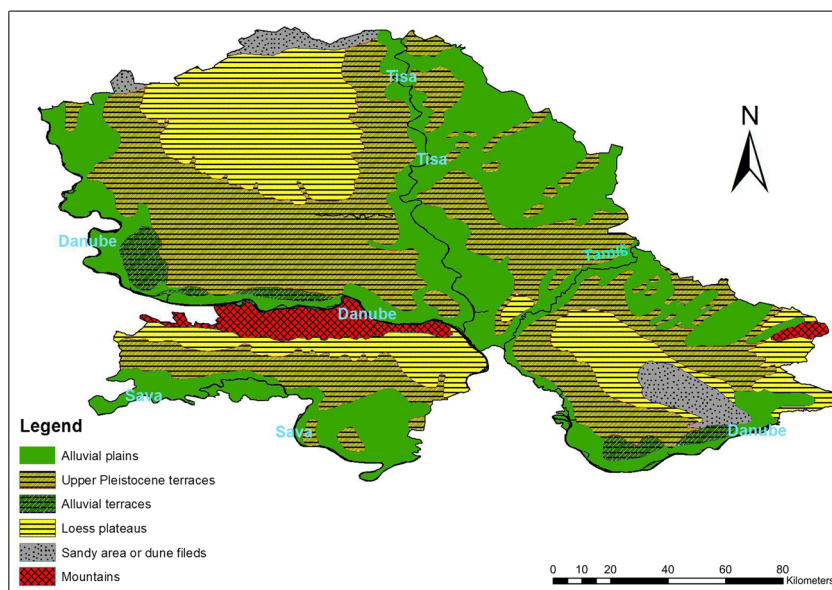

Fig. 3 Spatial distribution of Hg in soils of Vojvodina with shown cities that have more than 30,000 citizens

Fig. 4 Geomorphological map of Vojvodina (Bukurov 1972)

in soil formed on loess plateaus represents transit category between these two groups.

Average values of Hg concentrations for soils formed on different geomorphological units were 0.031 for sandy area with dune fields, 0.048 for alluvial terraces, 0.055 for upper Pleistocene terraces, 0.058 for loess plateaus, 0.083 for mountains and 0.092 mg kg^{-1} for alluvial plains.

When the samples were classified based on geomorphological units, a box-plot was produced to compare the variations among the six geomorphological units (Fig. 5). Soils from each unit have also shown some very high values (see the upper whiskers and points on Fig. 5 and the maximum values in Table 3) and very

low values (the lower whiskers on Fig. 5 and the minimum values in the Table 3) of total mercury content.

The coefficient of variation (CV) of soils from each geomorphological unit varied from 44.9 to 124.3 %, showing that there are significant variations in total mercury content within each geomorphological unit. Alluvial plains showed the highest values of CV (124.3 %), which is caused by the highest values of THg maximum content (0.974 mg kg^{-1}). Alluvial terraces and upper Pleistocene terraces have the lowest values of CV, which confirms that these soils are more homogenous than the soils formed on other geomorphological units.

Table 3 Statistical summary of total mercury content of mercury (mg kg^{-1}) in agricultural soils of Vojvodina Province, according to geomorphological units

	Sandy area dune fields	Alluvial terraces	Upper Pleistocene terraces	Loess plateaus	Mountains	Alluvial plains
Number of samples	43	35	519	286	48	439
Minimum value	0.008	0.011	0.022	0.013	0.030	0.015
Percentiles 25 %	0.012	0.033	0.039	0.041	0.037	0.043
Median	0.023	0.044	0.046	0.048	0.052	0.059
Percentiles 75 %	0.039	0.062	0.058	0.055	0.091	0.091
Maximum values	0.135	0.113	0.601	0.922	0.636	0.974
Average	*0.031 d*	*0.048 cd*	*0.055 cd*	*0.058 bc*	*0.083 ab*	*0.092 a*
Standard deviation	0.026	0.021	0.044	0.069	0.100	0.114
Coefficient of variation (%)	85.2	44.9	79.3	117.9	120.0	124.3
IQR[a]/median	1.165	0.667	0.411	0.313	1.039	0.817

Values in italics and marked with same letter do not differ on statistical significance for the level of importance $\alpha = 5$ % (according to the Duncan multiple range test)

[a] Inter-quartile range, difference between 75th and 25th percentiles

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Fig. 5 Box-plot graphical display of total mercury content (mg kg^{-1}) in agricultural soils of Vojvodina Province, according to geomorphological units
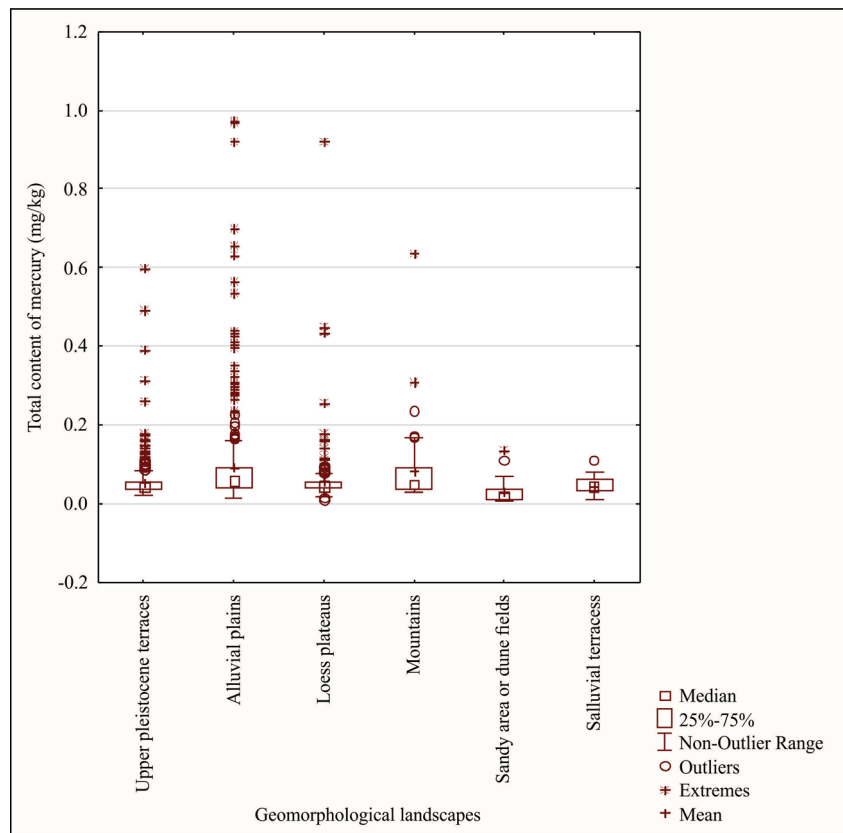
The effect of such an outlier can be removed by using a more robust measure of variation defined as the ratio between the inter-quartile range (IQR) and IQR/median for each dataset (Zhang et al. 2007). The highest values of IQR/median ratio were obtained for sandy area (1.165 mg kg^{-1}) and mountains (1.039 mg kg^{-1}), then alluvial plains (0.817 mg kg^{-1}), which indicates on large variability of THg content in these geomorphological units. Loess plateaus and upper Pleistocene terraces showed the smallest variation in THg content when this robust variation measure (IQR/Median) was applied (Table 3).

Content increase in soils formed on specific geomorphological units in the following order—sandy area < alluvial terraces < upper Pleistocene terraces < loess plateaus— can be explained by organic matter increase in these soils. However, it is not the case with soils formed on mountains and alluvial plains.

Higher concentration of Hg on alluvial plains indicated that the origin of Hg near rivers might be from anthropogenic source. The main rivers in Vojvodina, the Danube, the Tisa, the Sava and the Tamiš, have been dammed more than a century ago. Thus, higher concentrations of Hg in their alluvial plains out of narrow dammed zone around rivers must be related to natural and anthropogenic sources located in their huge catchments. An increase trend of Hg (aq) concentrations from the upstream to the downstream of the river was observed (Liu et al. 2012). This study highlights that the elevated levels of THg (aq) in surface water in industrial zone are a consequence of industrial and domestic sewage inputs. Domagalski (2001) found that methylmercury in sediment was the highest at a location with the greatest wetland land cover, in spite of lower total Hg at that site relative to other river sites. In the central Amazon region, erosion process due to deforestation and soil cultivation was marked as responsible for an important release of particulate Hg from the soil surfaces (Roulet et al. 1998). Evidence of human activity has proven in the Ebro delta, the largest wetland of Catalonia Spain, which reflects the accumulation of metals in the basin over many years, and on the Ebro headwaters (Rodriguez Martin et al. 2009). In addition, during flooding, the higher energy flows were capable of transporting bulk sediments of industrial and agricultural land in the Ebro River to the delta.

Higher Hg content in mountain region can be explained by high contents of clay in these soils, compared to chernozem, hydromorphic black soil and the alluvial soil, which jointly form 85 % of Vojvodina area. Same as with other heavy metals, the content and distribution of Hg in soil depend to a large extent on the parent material from which these soils had developed. Lithogenic elements are associated either with primary minerals or with secondary minerals (mainly clay minerals). In general, clays present negative charges and tend to undertake sorption of cations and are associated with Hg

retention in soil. Mean concentrations in Hg podzols, sandy soils and desert sands is 0.06, while the mean concentration in loamy soils is 0.13 mg kg^{-1} (Hooda, 2010). However, some studies found no statistically significant differences that indicated a direct influence of clay contents on soil Hg concentrations (Odumo et al. 2014).

Additional hotspots of Hg concentration of top soils are related to geographical locations of major towns such as: Novi Sad, Subotica, Zrenjanin, Sombor and Pančevo (Fig. 3). Higher content of Hg in soils of urban areas as a consequence of atmospheric deposition has been a subject of many papers (Yuan et al. 2014; Luo et al. 2008; Shi et al. 2013). Furthermore, anthropogenic inputs have also greatly contributed to an increase of Hg content in soil irrespective of either the physicochemical properties or the influence of the parent material (Rodriguez Martin et al. 2013).

Conclusions

Concentrations of Hg in agricultural soils of Vojvodina Province are within interval 0.008–0.974 mg kg^{-1}. The average concentrations of Hg is 0.068, with median 0.048 mg kg^{-1}. It was determined that Hg content is in statistically significant negative correlation with pH value, while there was not statistically significant correlation between contents of Hg and CaCO$_3$. The correlation of Hg concentration with organic matter contents in soil was determined.

Content of Hg coincides with the main geomorphological units of Vojvodina Province. Average values of Hg concentrations for soils formed on different geomorphological units were 0.031 for sandy area with dune fields, 0.048 for alluvial terraces, 0.055 for upper Pleistocene terraces, 0.058 for loess plateaus, 0.083 for mountains and 0.092 mg kg^{-1} for alluvial plains.

Hg spatial distribution confirmed that most of Vojvodina Province area has geochemical origin of Hg. Higher concentration Hg on alluvial plains indicated that the origin of Hg near rivers might be from anthropogenic source. The main rivers in Vojvodina have been dammed more than a century ago. Thus, higher concentrations of Hg in their alluvial plains out of narrow dammed zone around rivers must be related to natural and anthropogenic sources located in their huge catchments. Higher content of Hg in mountain regions can be explained with high contents of clay in these soils, compared to clay content in other parts of Vojvodina. Additional hotspots of Hg concentration of top soils are related to geographical locations of major towns.

The obtained results also indicated that the measured levels of Hg in the soil are not limiting factors for production of safe food in Vojvodina.

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