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MERCURY CONTENT IN AGRICULTURAL SOILS AND FIELD CROPS OF CENTRAL SERBIA

Jordana NINKOV*, Stanko MILIĆ, Jelena MARINKOVIĆ, Jovica VASIN, Branka MIJIĆ, Milorad ŽIVANOV, Dragana BJELIĆ

Institute of Field and Vegetable Crops, Serbia
*Corresponding author: jordana.ninkov@nsseme.com

Abstract

Mercury (Hg) is a heavy metal, designated as a pollutant in the environment, due to its harmful effects on biota. Mercury pollution is a significant global concern, not only due to its increased levels in the environment, but also due to its toxic effect on human health across the food chain. The aim of this study was to determine the content of Hg in agricultural soils and main field crops. Total number of 84 bulked soil samples were taken (0-30 cm depth) from agricultural land. At the same plots, 84 plant crops (11 species – used as food and feed) were taken during the vegetation season 2018. The samples were analyzed for total Hg content using Direct Mercury Analyzer DMA 80 Milestone. The obtained results of Hg content in soil were within interval 0.003-0.37 mg kg^{-1}. The average concentration of Hg was 0.08, with median 0.06±0.06 mg kg^{-1}. Obtained values of Hg in soils were below maximum allowable concentration (MAC) and this interval is complied with the most cited range in soils up to 1 mg kg^{-1} without known nearby contamination sources. It was found that Hg content is positively correlated with pH value, slit soil fraction, and $CaCO_3$. The obtained results of Hg content in plant – field crops, were within interval 0.0001-0.9087 µg kg^{-1}. Obtained maximum value is still far lower than MACs for feed and food. According to the average Hg content in plant species, obtained results were classified from highest to lowest, respectively: bean, alfalfa, maize, soybean, rapeseed, sunflower, barley, pepper, wheat, rye and tomato.

Keywords: *Mercury, Hg, Soil, Heavy metals, Field crops.*

Introduction

Mercury (Hg) has been listed as a high priority pollutant by many international organizations due to its mobility and persistence in the environments and high toxicity to organisms (Jiang et al., 2006). A global response to solving this problem has been finalized by the adoption of the Minamata Convention on Mercury. The Minamata Convention on Mercury was approved and signed in Geneva in 2013 and entered into force in 2017. It is an international treaty designed to protect human health and the environment from the harmful effects of mercury (UNEP, 2019). Control and monitoring of anthropogenically introduced Hg throughout its life cycle is the key factor in fulfilling the obligations set by the Convention, and the Republic of Serbia is a signatory country to the treaty.

Mercury is a metal that easily changes the aggregate state, it is volatile at 20^0C, and migrates easily through the environment and builds compounds of different toxicity to biota. 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. Over the past several centuries, mining has been the dominant anthropogenic source of Hg (Amos et al., 2015). Soil contamination with mercury due to mining was studied worldwide (Odumo et al., 2014). More directly, soil contamination can be the result of liquid or solid Hg sources disposal, such as accidental spilling, mine tailings, landfills, polluted sewage sludge, etc. (Leterme and Jacques, 2015).

Hg in soil occurs in several ionic species and it is susceptible to transformations through the various processes. Mercury could be introduced and accumulated in soil through various pathways. On the other hand, Hg from soil could be released into the atmosphere, thus soil becomes an important source of Hg (Shi et al., 2013). Methylmercury (MeHg) is bioavailable and can be bio-accumulated within food webs. Many studies have confirmed Hg biomagnification in the food chain (Krasinska and Falandysz, 2015).
The aim of this study was to determine the content of Hg in agricultural soils of central Serbia region and main field crops.

Material and Methods

Study was conducted as part of the Project: "Global assessment of the tolerance of field crops on dangerous and harmful substance in agricultural soil and irrigation water", which is supported by the Ministry of Agriculture, Forestry and Water Management of the Republic of Serbia in 2018.

Sample collection and processing

Field activities were carried out during the second half of 2018. The locations of collected samples of agricultural land are shown in Figure 1 and belong to 6 statistical districts of the Republic of Serbia: East, Bor, South, West, Belgrade and Central District. Total of 84 bulked soil samples were taken from topsoil 0-30 cm using a probe drill. One composite soil sample represented 15-25 subsamples from production plots (up to 5 ha area).
During field activities, total of 84 samples of plant material were taken also. Field and industrial crops were sampled after harvest as an average sample of seed from observed plot. Plots with forage crops were sampled immediately after cutting, as an average sample of aboveground part of alfalfa. Vegetable crops were collected as fresh samples of fruit (tomato and pepper), while bean was collected at the stage of mature seed as part of crops consumed in human diet. Samples of pepper and tomato were transported to the Laboratory in refrigerator cars.

Laboratory analysis

The pH value in 1:5 (V/V) suspension of soil in 1 mol/L KCl and water was determined using glass electrode according to ISO 10390 (2010). The carbonate content ($CaCO_3$ content) was determined according to ISO 10693 (1995) volumetric method. The organic matter content was measured by oxidation using the sulphochromic oxidation method by ISO 14235 (1998). Particle size distribution was determined in the <2 mm fraction by the pipette method (Van Reeuwijk, 2002). The size fractions were defined as clay (<2 μm), silt (2-20 μm), fine sand (20-200 μm) and coarse sand (200-2,000 μm).The soil and plant samples were analyzed for total mercury content using Direct Mercury Analyzer DMA 80 Milestone.

Statistical analysis

Data were statistically processed by analysis of the main descriptive parameters and correlation coefficients ($p \leq 0.05$) using STATISTICA for Windows version 12 (Dell Inc. 2016).

Results and Discussion

Mercury in soil

Obtained values of total mercury content in this study vary in a wide interval, from 0.003 to 0.37 mg kg^{-1}. The results fall into the interval that is most often cited for mercury content in the soil without a known nearby source of pollution, and which amounts to 0.01–1 mg kg^{-1} (Shi et al., 2013). Median value of mercury in this study is 0.06 mg kg^{-1}±0.06 (Table 1), which also complies with the most cited mercury content in worldwide soils of 0.06 mg kg^{-1} (Adriano, 2001). Obtained values match with national average for China soils of 0.065 and Liaoning Province of 0.064 mg kg^{-1} (Shi et al., 2013).

Based on analyses of 1,370 samples of agricultural soil of Vojvodina, median for this province of the Republic of Serbia is of somewhat lower value and amounts to 0.05 mg kg-1 (Ninkov et al., 2017). High variation of coefficient of variation CV (72.5%) points out high heterogeneity of tested soil samples (Table 1); but this value is lower than the obtained for studies in Vojvodina (CV=119.9%).

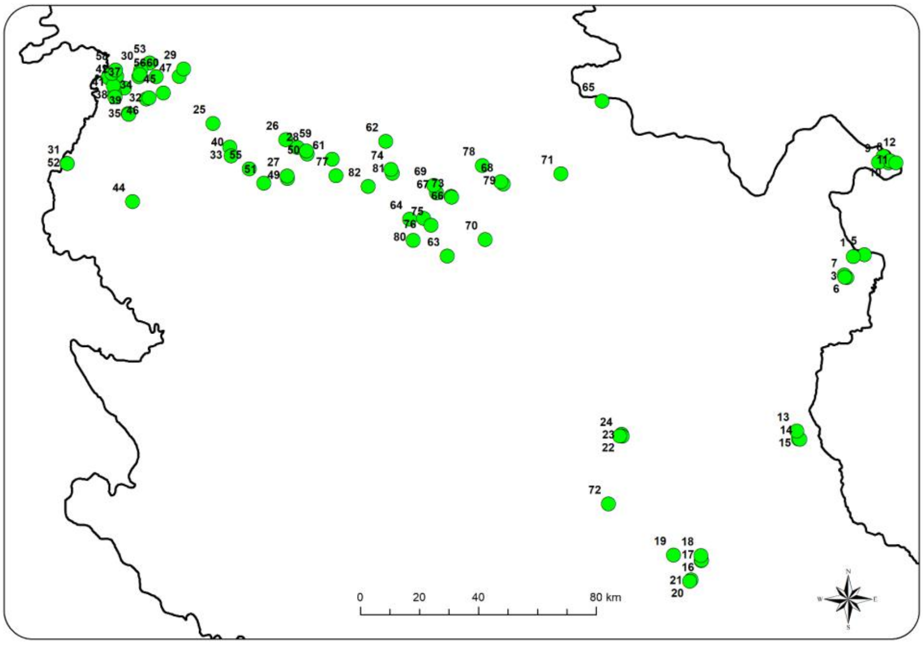

Figure 1. Layout of 84 taken soil and field crop samples in central Serbia

Based on GEMAS project (Ottesen et al., 2013), where 2,148 agricultural soil samples from a large part of Europe were analyzed (33 countries, 5.6 million km^2) at an average density of 1 sample site/2,500 km^2, median for mercury for agricultural arable land amounted to 0.03 mg kg^{-1} (Ap horizon, 0–20 cm). Median for Central Europe, where the Republic of Serbia belongs, amounted to 0.05 mg kg^{-1}. It was determined within GEMAS project that the values of Hg in Central Europe are the highest, compared to Scandinavia, Baltic Countries and Southern Europe. On the map of Hg distribution across Europe (Ottesen et al., 2013), part of Serbia, which is the subject of present study, ranged from 0.0476 to >1 mg kg^{-1}, while obtained values in our study are somewhat lower, i.e. Hg content in 25-75% percentiles were from 0.04 to 0.09 mg kg^{-1} (Table 1).
Mercury concentrations in soil of the United States of America ranged from 0.0091 to 0.37 mg kg^{-1} (Shacklette and Boerngen, 1984 *in* Wentz et al., 2014), similar to present research. Studies have shown that mercury concentrations in surface soil in the east part of USA are typically about twice those in the west part (Gustavsson and others, 2001 *in* Wentz et al., 2014). High mercury concentrations in the Eastern USA generally reflect greater rates of atmospheric mercury deposition in this region (Wentz et al., 2014).
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 Republic of Serbia (OG 23/1994). There is only one sample which is above of threshold limit of 0.3 mg kg^{-1} according to Decree on Limit Values in soil (OG 30/2018). The obtained results also indicated that the measured levels of Hg in the soil are not limiting factors for safe food production in Serbia.

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

Statistical parameters	Value
Number of samples	84
Minimum value	0.003
Percentiles 25%	0.04
Median	0.06
Percentiles 75%	0.09
Maximum values	0.37
Average	0.08
Standard deviation	0.06
Coefficient of variation (%)	72.47

Silt fraction content was in significant positive correlation with Hg content, while there were no positive statistically significant correlations with other soil fractions content (Table 2). Generally, as for the other elements, heavier soils have higher Hg content and lighter soils have lower Hg content. Mean concentrations of Hg in podzols, sandy soils and desert sands is 0.06, while the mean concentration in loamy soils is 0.13 mg kg^{-1} (Hooda, 2010). In general, clays present negative charges, tend to undertake sorption of cations, and are associated with Hg retention in soil. It was found that mercury and mercury salts can adsorb strongly to soil particles, particularly clay minerals and iron oxides within neutral pH range (He et al., 2015). According to Roulet et al. (1998), the fine fraction (<63 μm) was two to seven times more concentrated in Hg than the medium (63-210 μm) and coarse (> 210 μm) fractions. However, some studies found no statistically significant differences that indicated a direct influence of clay contents on Hg concentrations in soil (Odumo et al., 2014).

Table 2. Correlation coefficients between content of mercury (mg kg^{-1}), various size soil fractions (%) and basic soil chemical properties

	Coarse sand %	Fine sand %	Silt %	Clay %	pH in H_2O	pH in KCl	$CaCO_3$ %	Organic matter %
Hg	-0.065	-0.083	0.220*	-0.040	0.262*	0.274*	0.634*	0.175

clay (<2 μm), silt (2-20 μm), fine sand (20-200 μm), coarse sand (200-2,000 μm)
* p≤0.05, significantly correlated

According to the established correlations shown in Table 2, Hg content was in statistically significant positive correlation to pH value (both, active in H_2O and substitution in 1MKCl, acidity), and $CaCO_3$ content, while statistically significant correlation was not found with organic matter content. In the previous studies (Rodriguez Martin et al., 2009; Ninkov et al., 2017) negative correlation between pH value and Hg content was established. The both listed studies were on alkali soils, while observed soils in present research were mainly acidic soils with median value of pH 5.41±1.21. In the study of Rodriguez Martin et al. (2009), negative correlation of Hg with $CaCO_3$ was found, while in some studies (Rodriguez Martin et al. 2013; Ninkov et al., 2017) significant correlation between $CaCO_3$ and Hg content was not found.

Statistically significant correlation was not found between organic matter and Hg content, which is the opposite of previous studies (Rodriguez Martin et al. 2009, 2013; Shi et al. 2013; Ninkov et al., 2017). The strong link between Hg concentration and organic material content was also confirmed in study of Ottesen et al. (2013), especially in the relatively high Hg levels in the Scandinavian soils.

Mercury in plant materials

As the result of high sensitivity of Direct Mercury Analyzer that was used in present study, mercury was detected in all samples of plant material, but in very small concentrations. The highest value in the study was 0.9 μg kg^{-1} in maize (Table 3). This value is still 10 times lower than allowed for animal feed, which, according to the Rulebook on the quality of animal feed (OG 39/2016), amounts 0.1 mg kg^{-1}. According to Rulebook on food (OG 90/2018), the limit for mercury content in fresh fruit and vegetables is 20, and for cereals and flour 30 μg kg^{-1}, while values obtained in present study are far lower (Table 3). According to the average Hg content in plant species, obtained results were classified from highest to lowest, respectively: bean, alfalfa, maize, soybean, rapeseed, sunflower, barley, pepper, wheat, rye and tomato (Table 3).

Statistical importance was not determined in the relation of Hg content in the soil and plant material. The majority of observed samples included the seed that plant protects from accumulation of harmful substances as its own generative part. Besides, observed vegetables and alfalfa were exposed to atmospheric deposition of Hg. Results of Niu et al. (2013) study indicated that Hg concentrations in the leaves of lettuce, radish, alfalfa and perennial ryegrass were the function of air Hg concentrations and time.

Table 3. The concentration of Hg in plants (μg kg^{-1} of originally fresh matter)

μg kg^{-1}	wheat	barley	maize	soybean	sunflower	rapeseed	alfalfa	tomato
N	17	5	26	6	10	3	12	2
Min.	0.0001	0.0150	0.0001	0.0001	0.0001	0.0001	0.2818	0.0001
Max.	0.0552	0.0504	0.9087	0.0679	0.2252	0.0580	0.8519	0.0001
Average	0.0122	0.0285	0.0507	0.0322	0.0286	0.0307	0.5296	0.0001

N number of samples

N=1: Rye 0.0001; pepper 0.0131; bean 0.8416 μg kg^{-1}

Conclusions

The obtained results of Hg content in the soil were within interval 0.003-0.37 mg kg^{-1}. The average concentration of Hg was 0.08, with median 0.06±0.06 mg kg^{-1}. This interval complied with the most cited range in soils up to 1 mg kg^{-1} without known nearby contamination sources. It was found that Hg content is positively correlated with pH value, slit soil fraction, $CaCO_3$. The obtained results also indicated that the measured levels of Hg in the soil are not the limiting factor for safe food production in Serbia. The obtained results of Hg content in plant – field crops, were within interval 0.0001-0.9087 μg kg^{-1}. Obtained maximum value is still far lower than maximum allowable concentration for feed and food. According to the average Hg content in plant species, obtained results were classified from highest to lowest, respectively: bean, alfalfa, maize, soybean, rapeseed, sunflower, barley, pepper, wheat, rye and tomato.

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