Poll Res. 40 (1) : 34-39 (2021)

ISSN 0257–8050

MONITORING OF MERCURY CONTENT IN AGROECOSYSTEMS OF THE CENTRAL CHERNOZEM REGION OF RUSSIA

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(Received 30 June, 2020; accepted 22 August, 2020)

ABSTRACT

The paper considers the results of the local agroecological monitoring of the agroecosystems of the Belgorod region and the ecosystems of Yamskaya Steppe of the reserve "Belogorye". It was established that the total mercury content in the arable layer of chernozem of a typical heavy-loamy forest-steppe zone is on average 0.022 mg/kg and does not significantly differ from the element content in the black soil of a light clayey steppe zone (0.023 mg/kg). With an increase in the depth of the soil profile, the total mercury content is significantly reduced. Among the studied crops, the maximum concentration of mercury was found in the straw of maize and sunflower stalks (0.0104 mg/kg), and the minimum (0.0028 mg/kg) - in the hay of sainfoin.

KEY WORDS: Mercury, Agroecosystem, Soil, Black soil, Agricultural plants, Balance.

INTRODUCTION

The current environmental situation is aggravating both globally and regionally, so mankind is forced to seek effective measures for the sustainable development of the biosphere. One of the most powerful factors affecting the sustainability of agro ecosystems is the entry of heavy metals into them (Shcherbakov and Vasenev, 1996; Sokolov and Chernikov, 1999; Chernykh *et al*., 1999; Kabata-Pendias, 2011). From the practical point of view, one of the most important representatives of the heavy metals group is mercury, the content of which is normalized both in the soil and in food products.

Soil mercury content is the most important indicator characterizing the sanitary and hygienic situation since the accumulation in the soil of its excessive concentrations poses a direct threat to the environmental safety of the resulting agricultural products. Plants, absorbing mercury from the soil, accumulate it in the tissues, thus being an intermediate link in the chain: "soil - plant - animal - man." Therefore, control over mercury accumulation in agro-ecosystems is an important element of the state agro-environmental monitoring program, the results of which are used to develop environmentally friendly systems for fertilizing crops (Badin and Logoshina, 2019; Milovskikh *et al*., 2019; Sukhova *et al*., 2019).

Mercury in the plant body does not perform any biologically significant functions and is considered an absolute toxicant. The phytotoxicity of the element is primarily manifested in the suppression of the activity of the enzymes ribonuclease, catalase, oxidase and phosphatase (Chernykh and Ovcharenko, 2002; Dabakhov *et al*., 2005). According to G.N. Mhathre and S.B. Chaphekar, the harmful effects of mercury should be considered as a result of the complex disruption of many metabolic processes, in particular the formation of chlorophyll, photosynthesis, gas metabolism and respiration (Mhathre and Chaphekar, 1984). The key reaction explaining the suppression of metabolic processes in the plant organism is most likely the affinity of this element with sulfhydryl groups (Kabata-Pendias and Pendias, 1989). Symptoms of the poisoning of plants with mercury are delayed growth of seedlings and root development, inhibition of photosynthesis and, as a result, a decrease in yield (Titov, 2002). The accumulation of mercury in root tissues suppresses the penetration of potassium (K^+) into the aboveground plant organs, and it has been observed that in low concentrations mercury can act as a catalyst for the consumption process K^+ (Heenan and Campbell, 1980).

The main route of penetration of inorganic mercury from the environment into the human body is inhalation. Inorganic mercury is poorly absorbed in the human intestinal tract (not higher than 7%), whereas methyl mercury is absorbed by 95% regardless of the method of its intake. The most dangerous organic mercury compounds enter the body mainly with food and water (Poznyakovsky, 1996). Methylmercury usually has a sensory-motor effect, which manifests itself in gait disturbance, reduction of the visual field, difficulty in swallowing. Extremely sensitive to the action of mercury kidneys, which is caused by the affinity of their cells. Chronic mercury poisoning causes abnormalities in the central nervous system. Chronic mercury poisoning is manifested in the presence of asthenovegetative syndrome with pronounced tremor, mental disorders, tachycardia, labile pulse, as well as changes in the blood (Avtsyn *et al*., 1991). In the human body, the half-life of mercury varies from several months to several years. The lethal dose of mercury for humans when administered into the stomach is 0.2-0.5 g (Dabakov *et al*., 2005).

MATERIALS AND METHODS

As part of the study of the patterns of distribution of heavy metals, 22 sections of typical heavy loamy chernozem located in the Central Russian forest-steppe province and 22 sections of ordinary light clayous black soil located in the Central Russian province of steppe chernozem were studied. The average content of physical clay in the arable horizon of typical chernozem (Haplic Chernozems) was 56.8%, and ordinary chernozem (Calcic Chernozems) - 72.5%. The average thickness of the horizons of the soil profile, the content of soil organic matter and pH_{H_2O} values are presented in Table 1.

Laboratory studies were conducted in the accredited testing laboratory FSDI "Agrochemical Service Center "Belgorodsky" according to generally accepted methods. The content of mercury in soils, fertilizers and crops was determined by atomic absorption spectrometry. During statistical processing of the obtained test results, the values of average ($\bar{x}$), maximum and minimum (lim) element concentrations were calculated and confidence intervals were calculated for average values ($\pm t_{05}s$) and variation coefficients (V,%) (Dospekhov, 1979).

To determine the selectivity of the absorption of a chemical element by plants, a biological absorption coefficient was used, which is the quotient from dividing the number of elements in the plant ash by its total content in the soil. When calculating the coefficient of biological absorption, it was taken into account that the ash content in the absolutely dry matter of corn grain and straw is 1.5 and 7.3% respectively, sunflower seeds and stems 2.5 and 5.1%, soy beans and straw, 2 and 5.6%, alfalfa - 8.8%, sainfoin - 5.6%, clover - 8.5%, steppe grasses - 6.4%. The coefficient of biological absorption for the

Table 1. The average content of organic matter and pH_{H2O} in the profile of Haplic Chernozems and Calcic Chernozems

Genetichorizon	Average thickness of the horizon, cm	Content of organic matter, %	pH H_2O
Haplic Chernozems			
À topsoil depth	0–25	5.6	6.7
A	26-36	5.0	6.9
AB	37-90	3.6	7.5
B_Ca	91-111	2.1	8.0
BC_Ca	112-134	1.3	8.1
Cca	>135	1.0	8.1
Calcic Chernozems			
Ap	0-25	5.2	7.8
A	26-43	4.8	7.9
AB	44-72	4.1	7.9
B_Ca	73-90	2.9	8.1
BC_Ca	91-124	1.9	8.3
C_Ca	>125	1.6	8.3

steppe grasses was calculated taking into account the gross mercury content in the virgin chernozem of the Yamskaya Steppe of the reserve «Belogorie».

In the balance calculations, the data of the state statistics authorities in the Belgorod region on the application of organic and mineral fertilizers, ameliorants, acreage, and gross harvest of crops for 2010-2014 were used.

RESULTS AND DISCUSSION

In the process of studying the patterns of distribution of mercury in soils, it was found that the arable horizon of the black soil of a typical element (Haplic Chernozems) contains an average of 0.022, the common black soil (Calcic Chernozems) is 0.023 mg/kg, the content in the horizon $C_{cà}$ is 0.009 and 0.014 mg/kg respectively (Table 2).

The observed significant decrease in the total mercury content with depth is explained by its biophilic accumulation in the humus horizon with the formation of insoluble humates.

According to the results of our study, it was established that, on the whole, the gross mercury content in the arable soils of the forest-steppe zone and the arable lands in the steppe zone do not differ significantly.

The background content of mercury in a layer of 10–20 cm of the humus-accumulative horizon of virgin black soil typical (Haplic Chernozems) of «The Yamskaya Steppe» is 0.030 mg/kg respectively.

The results of surveys of arable soils of the Belgorod region showed that the total mercury content in them is lower than the established clarks. The content of the element in the soils studied by us is somewhat lower than the concentration noted in the reserved soils. Trends in the distribution of mercury across the depth of the soil profile are the same for arable soils and the soils of the Yamskaya Steppe of the reserve "Belogorye".

The approved value of the maximum allowable concentration in the soil of gross mercury is 2.1 mg/kg. The results of the study show that the mercury content in arable and virgin soils of the Belgorod region does not exceed the permissible concentrations.

The results of studies of the chemical composition of plant products showed that the maximum average concentration of mercury, amounting to 0.0104 mg/kg of absolutely dry matter, is observed in the by-products of maize and sunflower (Table 3). The minimum content of an element is noted in sainfoin hay (0.0028 mg/kg) and soybean grain (0.0032 mg/kg). Compared to crops, the steppe forbs of the protected zone is characterized by a significantly higher mercury content - 0.0126 mg/kg in terms of absolutely dry matter.

$\bar{x}$ For the ecological and toxicological assessment of coarse and succulent feeds in the Russian Federation, approved temporary maximum allowable levels are used, and feed grains are the technical regulations of the Customs Union 015/2011 "On grain safety". For food grains, the maximum permissible levels of toxic elements are

Table 2. Variational and statistical indicators of the total mercury content in the profile of typical chernozem (Haplic Chernozems), mg/kg.

Genetichorizon	$\pm t_{05}s$	lim	V,%
Haplic Chernozems			
A topsoil depth	0.022 ± 0.002	0.018 – 0.035	20.3
A	0.018 ± 0.002	0.008 – 0.030	29.3
AB	0.014 ± 0.001	0.010 – 0.022	21.0
$B_{C}a$	0.012 ± 0.001	0.008 – 0.020	24.0
$BC_{C}a$	0.010 ± 0.001	0.006 – 0.017	24.7
$C_{C}a$	0.009 ± 0.001	0.005 – 0.013	20.9
Calcic Chernozems			
À topsoil depth	0.023 ± 0.002	0.015 – 0.035	23.4
A	0.021 ± 0.003	0.013 – 0.032	28.5
AB	0.019 ± 0.003	0.010 – 0.030	31.6
B_{Ca}	0.018 ± 0.003	0.008 – 0.028	35.0
BC_{Ca}	0.015 ± 0.002	0.007 – 0.027	35.6
C_{Ca}	0.014 ± 0.002	0.006 – 0.027	36.8

established in the sanitary and epidemiological rules 2.3.2.1078-01 "Hygienic requirements for the safety and nutritional value of food products". According to the data of experiments, the concentration of mercury in perennial grasses, main and by-products of cereals and oilseeds does not exceed the permissible levels. It should be noted that mercury accumulates most strongly in the by-products of crops, and not in their reproductive organs.

The absorption of elements by plants is not always directly proportional to their content in the soil. The intensity of the absorption of elements by plants is determined by their selectivity, to identify which use the coefficient of biological absorption (Perelman, 1975).

Mercury is one of the most actively absorbed by the plant elements. The values of the coefficient of biological absorption of this element for crops and steppe grasses vary greatly (Table 4). The maximum value of the coefficient of biological absorption of mercury reaches 10.4 in the corn grain. The minimum rates of biological absorption of mercury (1.7) differ from alfalfa and clover. The steppe forbs are characterized by a relatively high value of the coefficient of biological absorption of mercury (6.6).

Biological absorption of mercury by vegetation determines its distribution over the soil profile: the higher the coefficient of biological absorption, the greater the content of the element in the humus-accumulative horizon with respect to the soil-forming rock (accumulation factor) (Protasova and Shcherbakov, 2003). The obtained value of the accumulation coefficient of this element in typical chernozem corresponds to 1.3.

The economic balance of mercury in agro ecosystems, which is part of the total biological circulation of substances, is calculated by comparing the amount of an element entering the soil with fertilizers and seeds of crops, with its expenditure on crop production and losses due to water erosion.

In the Belgorod region, organic fertilizers are considered to be the main source of mercury input into agroecosystems. In a much smaller quantity, this element is introduced with mineral fertilizers, ameliorants and seeds of crops used in agricultural production.

Table 3. Variational and statistical indicators of mercury content in crops and steppe grasses, mg/kg of absolutely dry matter.

Crop		$\bar{x} \pm t_{05} s \bar{x}$	lim	V, %
Corn	Grain	0.0036 ± 0.0005	0.0015 - 0.0050	30.6
	Straw	0.0104 ± 0.0005	0.0090 - 0.0120	11.0
Soy	Grain	0.0032 ± 0.0004	0.0010 - 0.0045	27.4
	Straw	0.0093 ± 0.0005	0.0077 - 0.0110	11.9
Sunflower	Seeds	0.0038 ± 0.0003	0.0021 - 0.0050	19.1
	Stems	0.0104 ± 0.0007	0.0080 - 0.0120	14.1
Lucerne	Hay	0.0035 ± 0.0003	0.0025 - 0.0047	16.5
Sainfoin	Hay	0.0028 ± 0.0004	0.0017 - 0.0043	29.7
Clover	Hay	0.0034 ± 0.0002	0.0023 - 0.0046	14.8
Steppe grasses	Hay	0.0126 ± 0.0010	0.0100 - 0.0160	17.2

Table 4. Biological absorption coefficients of mercury by plants (mg/kg ash) / (mg/kg soil).

Corn		Soybean		Sunflower		Lucerne	Sainfoin	Clover	Steppe
grain	straw	grain	straw	seeds	stems	hay	hay	hay	grasses hay
10,4	6,2	2,7	7,2	6,6	8,9	1,7	2,2	1,7	6,6

Table 5. Variational and statistical indicators of mercury content in organic fertilizers and ameliorants, mg/kg.

Organic fertilizer	$\bar{x} \pm t_{05} s\bar{x}$	lim	V, %
Manure runoff (2.22% dry matter)	0.0011 ± 0.0001	0.0007 - 0.0018	25.9
Straw compost (56% dry matter)	0.0044 ± 0.0007	0.0019 - 0.0078	34.0
Cattle manure (25% solids)	0.0066 ± 0.0011	0.0033 - 0.0108	36.7
Defecate (87% dry matter)	0.0136 ± 0.0010	0.0052 - 0.0204	33.2

Table 6. Economic balance of mercury in agroecosystems of the Belgorod region for 2010-2014

Balance sheet items		Hg
Intake, g/ha	organic fertilizers	0.032
	mineral fertilizers	0.004
	ameliorants	0.005
	seeds	0.001
	Total	**0.042**
Consumption, g / ha	takeaway with harvest	0.028
	soil erosion losses	0.044
	Total	**0.072**
Balance, ± g/ha	-0,03	
Intensity of balance,%	58.3	

Ammonium nitrate and azophoska predominate in the structure of application of mineral fertilizers in the region, and among the ameliorants there are defects. According to our data, the content of mercury in ammonium nitrate is 005 mg/kg, in azophoska - 0.028 mg/kg, in defecates - 0.0166 mg/kg (Table 5).

Organic fertilizers used on the territory of the region differ greatly in the content and ratio of chemical elements in them, which is a consequence of the characteristics of feeding and keeping of animals, as well as the removal and storage of organic fertilizers. For example, the average nitrogen content of the initial moisture content in manure (pig) manure is on average 0.28%, in cattle manure - 0.72%, in composts based on bird droppings - 2.84%. To add a nitrogen dose of 100 kg/ha with organic fertilizers, about 35.7 t/ha of manure runoff, 13.9 t/ha of cattle manure, 3.5 t/ha of straw compost and with this amount of organic matter will be applied to the soil 0.039, 0.092, 0.015 g / ha of mercury, respectively. Thus, with the same nitrogen dose of organic fertilizers, most mercury is introduced into the soil with cattle manure.

During 2010-2014, an average of 4.82 t/ha of organic fertilizers (in terms of cattle manure), 97.9 kg of the active substance of mineral fertilizers and 0.39 t/ha of ameliorants were applied on the territory of the Belgorod region. With this amount of agrochemicals, 0.032, 0.004 and 0.005 g / ha of mercury enter the soil (Table 6). A small contribution to the balance sheet entry is made by the seeds of cultivated crops. The proportion of mercury that comes with seeds is only 2.4% (0.001 g/ha).

The main expenditure item of the balance is the loss of an element with soil being washed away as a result of water erosion. According to some estimates, 3,235 thousand tons of soil (1.92 t/ha) is washed off annually in the region. Thus, the amount of leachable mercury with soil erosion losses is 0.044 g / ha.

A certain amount of mercury released into the soil is used by plants and is alienated from the economically valuable part of the crop. However, with crop production, compared with erosion losses, this element is carried out much less.

The research results showed that a negative economic balance is formed for the toxic element in question. The magnitude of the intensity of the balance of mercury is high and amounts to 58.3%.

CONCLUSION

Thus, the gross mercury content in the arable layer of chernozem of a typical heavy-loamy forest-steppe zone is on average 0.022 mg/kg and does not significantly differ from the element content in the black soil of a light clayey steppe zone (0.023 mg/kg). With an increase in the depth of the soil profile, the total mercury content is significantly reduced. Among the studied crops, the maximum concentration of mercury was found in the straw of maize and sunflower stalks (0.0104 mg/kg), and the minimum (0.0028 mg/kg) - in the hay of sainfoin. Mercury is most strongly accumulated in crop by-products, and not in their reproductive organs. The coefficient of biological absorption of mercury varies from 1.7 to 10.4. The main source of its income in agroecosystems are organic fertilizers. 76.2% of this element is paid with them.

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