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Monitoring of the content of manganese in soils and agricultural plants of the central Chernozem Region of Russia

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Abstract

The paper deals with the analysis of long-term observations of the manganese distribution in the soils of the south-western part of the Central Chernozem region of Russia in the Belgorod region. The soil mantle of the survey area is represented mainly by typical chernozem soil, leached chernozem soil and common chernozem soil. It has been found according to the results of a continuous agrochemical survey that 56.4% of cultivated soils belongs to the category with moderate supply of movable manganese, and 38.7% - to the category with low supply. It has been noted that among the main legumes white lupine has a very high ability to absorb manganese. The average content of this metal in its grain is 1065 mg / kg, which is 44 times more than in soybeans and 120 times more than in peas. Among man-made sources of manganese in agrocenoses, organic fertilizers are the main ones.

Keywords: manganese, soil, chernozem, soybean, pea, white lupine

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INTRODUCTION

The experience of scientific research in the field of mineral nutrition of plants suggests that the yields and quality of plant products significantly depend on the provision of soil with digestible forms of trace elements. High farming standards are characterized by attention not only to such common nutrients as nitrogen, phosphorus, and potassium, but also to other elements contained in soils in much smaller quantities. Trace elements are necessary for plants in very small quantities, but their lack or excess leads to serious changes in the process of metabolism (Kabata-Pendias 2011).

An important trace element is manganese. It participates in photosynthesis, respiration, nitrogen assimilation, water retention in cells, activation of enzymes, affects the metabolism in the process of mineral nutrition. Manganese is a poorly recyclable element, and young leaves suffer primarily from its deficiency: cereals are affected by gray spot (inter-vein chlorosis), leguminous seeds are covered with black and brown spots. Photosynthetic dysfunctions lead to chlorosis of leaf tissues and their subsequent death, which ultimately can lead not only to a reduction of yields, but also to the absence of fruiting. In Russia, including the Central Chernozem Region (CCR), there is a lot of arable soils with low providing with manganese (Kaigorodov and Piskunova 2017, Kuzmichev et al. 2018, Poddubny 2018).

An excess of manganese is also harmful. The toxicity of this element leads to inhibition and even death of plants: the growth stops, the leaves become smaller and chlorosis appears, the stems become brittle due to the death of the outer tissues. Especially brightly the excess element appears in acidic soils and at high humidity (Petrov and Seliverstov 1998, Reay and Waugh 1981, Zornoza et al. 2010).

Manganese compounds for soil condition is of great value, because this element is not only vital for plants, it also controls the behavior of a number of other nutrients, for example, the availability of manganese and associated nutrients decreases under oxidizing conditions (McKenzie et al. 1977, 1980). Such land-reclamation as soil liming can lead to a significant change in the content of mobile manganese in the soil (Dubovik 2009).

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Manganese in the soil environment is uneven: its presence is connected with the content in the mother rock and emissions of metallurgical and glass factories, thermal power plants (Fiala et al. 2013, Kula et al. 2018). So, near the ferroalloy production plants, the total element content reaches 4600 mg / kg of soil (Mihaileanu et al. 2018, Pavilonis et al. 2014).

According to the category of toxicity among heavy metals, manganese belongs to moderately hazardous substance. The maximum permissible concentration (MPC) of gross manganese in the soil, as defined by Russian legislation, is 1500 mg / kg.

The object of this paper is to study the dynamics of the content and distribution of manganese in soils and concentration in agricultural plants.

RESEARCH METHODOLOGY

The survey was conducted in the southwestern part of the Central Chernozem Reserve in the territory of the Belgorod Region, which is located in two soil zones: forest-steppe and steppe. The forest-steppe zone covers about 75% of the area, dominated by typical chernozem (Haplic Chernozems) and leached chernozem (Luvic Chernozems). The soil cover of the steppe zone is mainly represented by ordinary chernozem (Calcic Chernozems).

The article presents materials of continuous agrochemical survey of arable soils, as well as data of local agroecological monitoring at reference soil lots on the state of agrocenoses of the Belgorod Region. At these sites there was selected plant production: the samples of white lupine, soybeans, peas, and alfalfa hay, sainfoin and clover. The reference areas (4-40 hectares) are located in almost all administrative districts of the region in the forest-steppe zone.

The laying of soil cuts and sampling were carried out within the framework of separately conducted survey in the forest steppe (typical black soil) and steppe (ordinary black soil) zones of the Belgorod region.

Investigational analysis was conducted in an accredited testing laboratory of the Federal State Budgetary Institution “Center of Agrochemical Service “Belgorod”. Mobile forms were extracted with ammonium acetate buffer (AAB) with pH 4.8. The determination of the total manganese content was carried out by atomic absorption spectrometry.

To determine the selectivity of the absorption of chemical elements by plants, a biological absorption coefficient (BAC) was used, which is the quotient from dividing the number of elements in the plant ash by its total content in the soil.

Statistical processing of the obtained test results included the calculation of the confidence interval for the mean values ($\bar{x}$±$t_{05}s\bar{x}$) and coefficient of variation (V, %).

RESULTS AND DISCUSSION

Manganese is one of the most common elements in the lithosphere, its clarke (average content) in the soils of Russia is 850 mg / kg, in the soils of the world - 488 mg / kg (Kabata-Pendias 2011).

According to the results of studies of the black soils of the Central Chernozem Region, the highest content of Mn in the surface soil layers is characterized by ordinary chernozem – 733 mg / kg, somewhat less than this metal in typical chernozem – 680 mg / kg (Gorbunova et al. 2008, Protasova and Shcherbakov 2003).

According to the results of the background agroecological monitoring, it was established that the upper layers of typical chernozem reserve (in the territory of the Yamskaya Steppe area of the Belogorye State Reserve) and ordinary (Rovensky Natural Park) contain the highest content of manganese, the metal content in the latter is higher by 27.4% (442 vs 321 mg / kg soil). The content of the element decreases down the profile.

A similar situation is observed in arable soils. The maximum values were recorded in the upper soil layers (0–25 cm) of typical and ordinary chernozems and amounted to 345 and 397 mg / kg, respectively (**Table 1**).

It should be noted that ordinary chernozem was formed on carbonate loess-like clays of heavier granulometric texture, and highly dispersed minerals in the clay fraction contribute to the fixation of this element. Also, due to the greater degree of carbonation, the ordinary chernozem has a high redox potential - this leads manganese to a state inaccessible to plants (Mn^{4+}, Mn^{3+}). In soils where a weak alkaline environment prevails, Mn turns into a form that is for plants hard-to-reach (McKenzie et al. 1977, 1980).

The intraprofile distribution of manganese in soils is characterized by a decrease in the concentration of the indicated chemical element with depth increasing. The minimum amount of manganese is in soil-forming rocks at a depth of more than 125 cm and averages 234 mg / kg of soil for the reference areas of the forest-steppe zone, 287 mg / kg for the steppe zone.

Since the oxidized forms of manganese are unavailable to plants, the definition of its mobile forms is of great value for soil manganese supply assessment. According to the results of the research, it has been established that the soil supply with readily available forms of this element has a slightly different distribution pattern in the soil profile, namely: in the typical chernozem, there are 2 maxima (in the arable horizon and underlying rock), and in the ordinary chernozem – the growth of mobile manganese content with depth (see **Table 1**).

Topsoil has significant (4 times) differences in the content of mobile forms of this chemical element: 16.7 mg / kg in typical chernozem and 4.1 mg / kg in ordinary

Table 1. Variational and Statistical Indicators of the Manganese Concentration in Typical Chernozem and Ordinary Chernozem, mg / kg

Genetic horizon	Average depth of horizon, cm	Total			The level of mobile fraction		
		$\bar{x}\pm t_{05}s\bar{x}$	lim	V, %	$\bar{x}\pm t_{05}s\bar{x}$	lim	V, %
Typical Chernozem							
Ap	0-25	345±14.6	245-396	9.6	16.7±3.4	6.2-35.2	46.2
A	26-36	329±15.9	254-393	10.9	12.5±2.2	5.4-23.8	39.6
AB	47-90	308±17.0	241-383	12.4	9.2±1.3	3.9-17.3	30.7
B_{Ca}	91-111	256±19.4	154-321	17.1	12.1±2.0	4.9-20.9	36.5
BC_{Ca}	112-134	234±18.8	175-328	18.1	16.4±2.5	6.7-33.6	34.2
C_{Ca}	> 135	239±28.4	123-406	26.8	17.0±3.3	0.0-34.4	43.4
Ordinary Chernozem							
Ap	0-25	397±17.9	311-463	10.2	4.1±0.7	1.5-7.2	37.9
A	26-43	390±16.9	315-445	9.8	3.7±0.6	1.2-6.2	36.2
AB	44-72	363±21.8	246-434	13.5	4.3±0.9	1.5-9.6	45.9
B_{Ca}	73-90	327±19.6	238-420	13.5	7.0±1.5	2.6-15.0	47.4
BC_{Ca}	91-124	287±16.2	225-387	12.7	10.2±1.7	1.8-21.2	38.1
C_{Ca}	> 125	279±10.3	233-327	8.3	11.0±1.0	4.5-14.8	21.0

Table 2. The Dynamics of the Distribution of Arable Soils of the Belgorod Region on the Content of Mobile Forms of Manganese, % of the Surveyed Area

Years	Soil classification according to mobile manganese, mg/kg of the soil			Weighted mean concentration, mg /kg
	low < 10	moderate 10-20	high > 20	
1990-1994	25.1	44.5	30.4	17.5
1995-1999	45.0	44.2	10.8	12.1
2000-2004	65.7	31.1	3.2	9.8
2005-2009	64.4	35.0	0.6	9.3
2010-2014	53.6	42.4	4.0	10.3
2015-2018	38.7	56.4	4.9	11.7

Table 3. Manganese Content in Plant Products, mg / kg of Absolutely Anhydrous Substance

Crop		$\bar{x}\pm t_{05}s\bar{x}$	lim	V, %
White lupine	grain	1065±170	659-1640	32.2
	straw	833±138	594-1407	32.4
Soybeans	grain	24.1±1.15	16.9-27.9	10.8
	straw	12.4±1.10	7.50-17.6	20.0
Pea	grain	8.91±0.22	7.85-9.84	5.5
	straw	18.0±1.67	7.76-22.5	21.0
Clover	hay	31.2±1.69	24.5-37.6	12.3
Esparcet	hay	30.7±0.97	27.4-34.9	7.1
Lucerne	hay	28.5±1.48	22.9-37.5	11.8

chernozem. This is explained by the greater degree of acidity of the typical chernozem and the increased ability of Mn to become accessible to plants. The mobility of manganese in the soil contributes to pH decrease in soil (Wilson 2005). With greater gross manganese supply, ordinary chernozem is characterized by a lower saturation of its mobile forms: about 4.8% of its total amount for typical chernozem and 1.0% for ordinary chernozem. A significant part of manganese is represented by poorly soluble forms and is not available for plants.

The amount of mobile manganese in soils depends on the reaction of the environment, oxidation-reduction potential, total content, particle size distribution, conditions of moistening (Pobilat and Voloshin 2017). The Belgorod region refers to the areas with a temperate continental climate, transitional from more humid climates in the western regions (the Prokhorovsky district), and insufficiently humid in the south-east (the Rovensky district) (Shcheglov et al. 2012).

According to the results of a continuous agrochemical survey, the highest weighted average content of mobile manganese in arable soils of the region was recorded (17.5 mg / kg) in 1990-1994. Then the indicator took a downward trend and reached a minimum (9.2 mg / kg) in 2005–2009. This situation has arisen in connection with the reduction of manganese supply in the agrocenoses with fertilizers and the removal of the element of commodity crop production. In 2010-2014 there was a slight increase in this parameter to 10.3 mg / kg, and in 2015-2018 – up to 11.7 mg / kg. According to the last cycle of the agrochemical survey, more than one third of the soils being surveyed on the content of mobile manganese belong to the category with low-content of this element, more than half are characterized by the average availability of this substance (**Table 2**).

The maximum permissible concentration of mobile manganese (140 mg / kg) was not recorded in the region during the observation period. Soil saturation with the specified chemical element continues to be insufficient.

The survey determined the content of manganese in the main crops in the field of legumes. According to the results of local agroecological monitoring of crop production, there was a high content of manganese in white lupine: 1065 mg / kg in grain and 833 mg / kg in straw (**Table 3**). White lupine has a very high ability to absorb manganese (Lukin 2018). It has been found that

Table 4. Average Manganese Concentration in Ashes and Biological Absorption Factor

Crop		Average ash, % of absolutely dry substance	Average ash value, mg/kg of ash	Biological absorption factor, (mg/kg of ash) / (mg/kg of soil)
White lupine	grain	4.2	25357	73.5
	straw	6.2	13435	39.0
Soybeans	grain	5.2	463	1.34
	straw	5.6	221	0.64
Pea	grain	3.1	287	0.83
	straw	8.0	225	0.65
Clover	hay	8.5	367	1.06
Esparcet	hay	5.6	548	1.59
Lucerne	hay	8.8	324	0.94

the hyper-accumulation of manganese in plant tissues does not cause any signs of physiological stress (Fernando et al. 2006, Kula et al. 2018, Xue et al. 2015). According to the test center of the All-Russian Institute of Poultry Farming Institute, the depositing of manganese in various varieties of white lupine breeding of RSAU – Moscow Agricultural Academy named after K.A. Timiryazev, may be in the range from 326 to 1396 mg / kg (Andrianova et al. 2015). The content of this element in soybean grain was significantly lower and amounted to 24.1, in pea – 8.91 mg / kg. Perennial leguminous forage grasses contain approximately the same amount (28.5-31.2 mg / kg) of this substance.

The existing legislation does not standardize the maximum content of manganese in human food and feed for farm animals.

The absorption of elements by plants is not always directly proportional to their content in the soil. The physical and chemical properties of the soil, such as pH and buffering – the resistance of the soil to acidifying factors of anthropogenic origin, largely affect the absorption of manganese by the plants (Murawska et al. 2017). The intensity of the absorption of elements by plants is determined by their selectivity, for the quantitative characteristics of which the coefficient of biological absorption is used (**Table 4**) (Spitsyn et al. 2013).

The value of BCF for crops varies greatly. The maximum values of BCF for this element are recorded in white lupine: 73.5 in grain and 39.0 in straw. BCF minimum values were typical for pea: 0.83 in grain, 0.65 in straw.

Deep subsoils are the main natural source of manganese in soils. Among the anthropogenic sources of this element are organic fertilizers. Due to the implementation of programs for the development of pigstry and poultry in the region, the volume of organic fertilizers used is growing. So, in 2005-2009 the level of their introduction amounted to only 1.2 t / ha of sown area, it increased to 4.8 in 2010-2014, and amounted to 7.8 t / ha in 2015-2018. Depending on the type of organic fertilizer, the average manganese concentration in it is different. Most of the manganese is contained in straw compost (56% of dry substance) – 128 mg / kg, in cattle manure (25% of dry substance) - 44.7 mg / kg, pig manure waste (2.22% of dry substance) - 3.3 mg / kg.

An insignificant amount of this metal as a concomitant element is introduced into agrocoenosis with mineral fertilizers.

CONCLUSIONS

According to the results of long-term observations of agrocoenosis, it was established that during 2010-2018 an increase in the content of mobile forms of manganese in arable soils was observed. The weighted mean of it according to the existing gradation refers to the average value. Excess of maximum permissible levels of mobile manganese in soils was not observed. The main anthropogenic source of manganese in the agrocoenosis are organic fertilizers, the level of application of which reached a record figure in the last survey cycle – 7.8 t / ha of sown area. From the main cultivated crops in the field of legumes, white lupine is characterized by a very high content of manganese in the grain. The least intense accumulation of this element occurs in the soybean and pea straw.

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