Content of heavy metals in Haplic Chernozem under conditions of agrogenesis

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Abstract. The paper presents the results of a long-term study on the content and distribution of heavy metals in Haplic Chernozem of agrocenoses in southern zone of Rostov Region. The impact of various agricultural technologies - traditional (using moldboard ploughing) and resource-saving (minimum and No-till) on accumulation and mobility of Pb, Zn, Cu in Haplic Chernozem in winter wheat cultivation is considered. The total content of Pb, Zn, Cu in the winter wheat areas corresponds to the background level and does not exceed permissible concentrations. Low mobility of elements (Pb - 2.0-3.0%; Zn and Cu up to 1.0% as a percentage of their total forms) is a regional soil feature. In addition, the low availability of Zn and Cu in soils is due to their removal with the crops in the absence of micronutrient fertilizer replenishment. The significant role of soil organic matter in the accumulation of both total and mobile forms of heavy metals in soil has been confirmed. The intensity of the cultivation methods used has a significant effect on the total content of Zn, Cu and on the mobility of Pb, Zn, Cu in Haplic Chernozem.

1 Introduction

Soil is one of the most important natural resources. Anthropogenic pressure on soils is often accompanied by their degradation, including pollution by heavy metals. Among the many anthropogenic factors affecting the change in the content of heavy metals in the soil, crop production technologies play a significant role. Intensive farming contributes to a change in the content of metal compounds in the soil, which can negatively affect crop quality, both due to its decline caused by insufficient micronutrition and due to contamination of products with highly dangerous substances [1]. The content and composition of heavy metals in agricultural soils is largely determined by the source material (parent rock). But their entry from other sources, including organic and mineral fertilizers, chemical ameliorants can be significant [2]. Widespread application of advanced resource-saving technologies based on minimal tillage is a pressing issue. However, it is the least studied under the soil and climatic conditions of Rostov Region. The introduction of resource-saving technologies is possible with high farming standards, sufficient supply of fertilizers and pesticides. To determine the content of heavy metals in soils taking into account their regional characteristics and the

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intensity of modern agricultural technologies is necessary for assessing and predicting the availability of macro- and microelements to plants, and environmental monitoring.

2 Materials and methods

Field research studies have been carried out for 3 years (2014 - 2017) on the premises S. M. Kirov JSC in Peschanokopsky district of Rostov Region where minimum tillage technology has been used since 2000, No-till has been applied since 2008. In terms of natural and economic division, this territory belongs to the Southern Haplic Chernozems (Ciscaucasia) with a semi-arid climate, moderately hot summers and moderately cold winters. According to the World Reference Base for Soil Resources (WRB), this type of chernozem belongs to Calcic Chernozems [3].

Nine soil profiles were laid in the winter wheat areas: 4 – using No-till (Semeato TDNG-420 made in Brazil); 4 – minimal cultivation to a depth of 10-12 cm (heavy disk harrow-3); 1 – moldboard ploughing (ploughing to a depth of 25-27 cm, lift-type disc plough-4-35). Soil samples from two soil profiles in the virgin area were compared.

To determine the mobile forms of Zn, Cu, Pb in the soil acetate–ammonium buffer solution (pH 4.8) was used followed by atomic absorption spectrometry (soil to solution ratio 1:10) [4]. The total content of elements was determined by X-ray fluorescent (XRF) scanning spectrometer SPECTROSCANMAX-GV.

Mathematical processing of the results was carried out by correlation analysis and ANOVA methods using the STATISTICA 10 software package.

3 Results and discussion

It was established that lead accumulated in the humus horizon (Ad, A), decreased down the profile accumulating in the lower horizons - Bea and C (Figure 1a). The organophilicity of Pb is well known. According to Morin [5], the content of lead in the silt fraction of contaminated humic soil (Corg = 6.4%) in northern France reached 80%. In arable soil with a low content (Corg = 1.5%), the fraction of Pb-humates was lower, it constituted only 35%. The accumulation of total Pb content in the lower horizons of the soil profile was due to its binding by carbonates. Zn and Cu were characterized by a uniform distribution over the entire soil profile (Figure 2a and Figure 3a).

The total Zn content in the upper humus horizon(Ad) of Haplic Chernozem ranged from 71.8 to 88.3 mg/kg, Cu - 41.6 - 54.2 mg/kg, Pb - 25.3 - 31.9 mg/kg, which corresponded to the background level in this region [6, 7].

Ecotoxicological assessment of the soil collected from winter wheat areas and virgin land showed no excess of the approximately permissible concentrations of the studied elements [8].

More reliable information on the content and impact of trace elements on the ecological status of agrocenoses was provided by their mobile forms. The content of mobile compounds of the elements under study can be represented in the form of a decreasing series: Pb> Zn> Cu. The percentage of mobile elements was Pb - 2.0-3.0%; Zn and Cu up to 1.0% of the percentage of their total content. According to agrochemical standards, soil is characterized by a low availability of mobile compounds of Zn (<2.0 mg/kg) and Cu (<0.2 mg/kg) [9]. This is probably due to active absorption by plants and indicates insufficient use of zinc and copper-based fertilizers.

The low mobility of Cu and Zn in the soils of Rostov Region is due to the presence of carbonates, their highly dispersed micellar carbonates and a slightly alkaline reaction of the medium [6, 7].
Fig. 1. Profile distribution of lead in Haplic Chernozem (a) total, (b) mobile), mg/kg.

Fig. 2. Profile distribution of zinc in Haplic Chernozem (a) total, (b) mobile), mg/kg.
Soil is the major source for plants to intake Zn and Cu. The deficiency of these microelements deteriorates the quality of crop production, including the ratio between macro- and microelements [10]. These changes often cause animal and human diseases [11].

The use of resource-saving technologies, including No-till, with sufficiently large doses of mineral fertilizers and intensive care of crops increased the content of mobile Zn and Cu compounds in the soil, but the degree of availability remained the same.

ANOVA of the data obtained indicated a statistically significant effect of the cultivation method on the total content of Cu and Zn. Changes in total Pb content were insignificant. However, analysis of the mobile Pb content both on average in the soil profile and in the humus horizon (Ad-AB) showed a statistically significant effect of the intensity of the studied cultivation methods (Figure 4).
Fig. 4. The influence of a cultivation method on the content of mobile lead compounds in Haplic Chernozem (a) - on average in profile, (b) - and in the humus horizon (Ad-AB).
A significant effect of the intensity of the methods used on the content of mobile Zn compounds was revealed over the entire soil profile, and on the content of mobile Cu compounds - only in the soil humus horizon (Ad-AB) (Figure 5).
Soil organic matter (SOM) is one of the main components of the soil affecting the accumulation of heavy metals. A direct average dependence of the total Pb content ($r = 0.56$ at a confidence level of 0.95%) on the humus content was revealed (Figure 6a). A similar dependence ($r = 0.57$) was revealed for total Zn. Feedback has been found between the mobile Cu compounds and the humus content (Figure 6b).

**Fig. 6.** Dependence of the accumulation of lead (a) and copper (b) in Haplic Chernozem on humus content.
Cu is known to have affinity with the organic complex of the soil. Our previous studies have shown that the use of resource-saving technologies, including No-till, increased the humus content compared to ploughing [12]. According to Moreira [13], an increase in SOM concentration with No-till causes the decrease in the availability of Cu to plants. Therefore, when increasing the soil organic material in the fields it is necessary to apply copper-containing fertilizers.

4 Conclusion

The content and distribution throughout the profile of heavy metals (Pb, Zn, Cu) in Haplic Chernozem of agrocenoses in the southern zone of Rostov Region is due to regional soil characteristics and the intensity of cultivation methods.

Comparing the obtained results with current approximate permissible concentrations (APC), it should be noted that the content of heavy metals (Pb, Zn, Cu) when using both traditional and resource-saving technologies cannot cause any pathological changes or anomalies of biological processes or lead to their accumulation in agricultural plants.

SOM is one of the key factors determining the mobility of Pb, Zn, Cu in Haplic Chernozem. An increase in the content of SOM when using resource-saving technologies, including No-till, can reduce the availability of trace elements (Cu and Zn) to plants. To preserve soil fertility and improve the crop quality, introduction of both macro- and microelements is necessary when growing crops.

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