International Journal of Ecosystems and Ecology Science (IJEES) **Vol. 10 (4):** 603-608 (2020)
https://doi.org/10.31407/ijees https://doi.org/10.31407/ijees10.4

EFFECT OF FERTILIZERS SYSTEMS ON ACCUMULATION OF HEAVY METALS IN GRAY FOREST SOIL

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Received July 2020; Accepted August 2020; Published September 2020;

DOI: https://doi.org/10.31407/ijees10.404

ABSTRACT

Mobile forms content of plumbum and cadmium at systematic application of organic and mineral fertilizers in field crop rotation on gray forest soil has been investigated. It was found that the use of fertilizers affected the accumulation of these indicators in the soil relative to the initial state, but the maximum concentration of maximum permissible concentrations (MPC) was not observed. With the organic fertilizer system (60 t/ha of manure) there was a decrease in mobile plumbum by 33% compared to its initial content in the soil. However, it should be noted that the coefficient of technogenic concentration for plumbum was more than one (Kc> 1), which indicates the process of its accumulation in the soil to the background level. The highest indicator of the coefficient of technogenic concentration for plumbum (Kc = 2) was observed with the joint application of organic and mineral fertilizers (60 t/ha of manure + $N_{100}P_{60}K_{100}$). The distribution of mobile plumbum and cadmium according to the soil profile depended on the peculiarities of soil genesis - there was a tendency to increase stocks under agrochemical load in the norm $N_{100}P_{60}K_{100}$ against 60 t/ha of manure, in the lower part of illuvial humus and upper – illuvial horizons at a depth of 50–80 cm, as well as a decrease at the boundary of humus-eluvial and illuvial humus horizons – 25–45 cm. Studies of the content of mobile forms of plumbum and cadmium in the grain of winter wheat indicate the stability of levels of contamination by these elements of the grain within the permissible concentrations of MPC.

Keywords: heavy metal, soil, toxic effect, plants, soil fertility, fertilizers.

INTRODUCTION

Under modern conditions, the anthropogenic factor is one of the most important, the impact of which has led to the disruption of natural connections and flows of conversion of organic matter and energy, changing the conditions of the biological cycle of nutrients (Orlov, 1994; Litvinova et al., 2019; Demyanyuk et al., 2019). One of the negative consequences of these processes is the supernatural accumulation of heavy metals in the soil, which, in turn, determines the conditions of development and biochemical characteristics of agrophytocenosis **(**Raymond and Okieimen, 2011, Dal Corso, et al., 2019). Heavy metals are major pollutants in areas with high anthropogenic

pressure. The accumulation of heavy metals in soils is a concern in agricultural production. Mobile forms of metals can accumulate in the soil to high concentrations, which cause their toxicity to both soil biota and plants (Nagajyoti, Lee. & Sreekanth, 2010; Vhahangwele Masindi and Khathutshelo L. Muedi, 2018; Yadav, 2010).

Increased anthropopression in agrocenoses is associated with the use of mineral and organic fertilizers, pesticides. It is known that with fertilizers not only the main nutrients get to an agroecotope: nitrogen, phosphorus, potassium, etc., but also heavy metals which are considered as priority pollutants of biosphere (Dmitruk, 2006). It is known that the determining factor in the amount of chemical elements in soils is their content in the soil-forming rock (Larher, 1978; Lebedovsky, 2010) In the forest-steppe zone, it is mainly forests and forest-like loams. The content of elements inherited by soils from parent rocks changes under the influence of a set of factors that determine the conditions of soil formation in agrolandscapes (Bilyavsky and Butchenko, 2006).

The mobility of heavy metals depends on their content in ecosystems. It is believed that the content of mobile forms of metals determines the level of toxicity to biological objects and depends on many factors, primarily on the reaction of the soil environment, soil microbiome, humus content, moisture, etc. (Korsun, et al., 2013; Bondar, et al., 2019; Symochko., 2020). Thus, it was found that plumbum, compared to other heavy metals, is less mobile and mainly accumulates in the upper horizon of the soil cover. The mobility of cadmium in the soil depends on the environment and redox potential. Cadmium contamination of the soil is considered one of the most dangerous environmental phenomena, as it accumulates in plants above normal, even with low soil contamination. This research had as main objective to investigate the influence of systematic application of fertilizers in the field crop rotation on the accumulation of heavy metals in gray forest soil under different loads of mineral and organic fertilizers.

MATERIALS AND METHODS

The study was hold in a stationary research at the Agrochemistry Department of the National Scientific Center «Agriculture Institute of the National Academy of Agrarian Sciences of Ukraine». We studied the grey forest big-particles dust light-loam soil during the five-field crop rotation: grain maize, spring barley, buckwheat, pea, winter wheat.

An average sample (soil layer 0-20 cm) had following agrochemical parameters: pH_{KCL} – 4,6; hydrolyzed nitrogen content – 50,8 mg/kg of soil; mobile phosphorus compounds – 188 mg/kg of soil, mobile potassium compounds – 100,0 mg/kg of soil, humus content – 1,20 %. Original content Plumbum – 1,0 mg/kg, Cadmium – 0,10 mg/kg.

The experiment started in 2011 and took place in nature on three fields, with a four-time replication. The cultivation area was 52 m^2, the tested area under crops was 22 m^2.

Analytical works were carried out in soil samples taken for the period of completion of the first rotation of crop rotation for growing winter wheat (2016-2018). The rate of mineral fertilizers for winter wheat was $N_{100}P_{60}K_{100}$. Cattle's dung with litter was used for grain maize, one dose was 60 t/ha, or 12 t/ha if calculate for 1 hectare of crop rotation fields, the other crops used an afteraction: winter wheat – 4 year.

Concentration of mobile (after extraction with acetate-ammonium buffer solution pH 4.8) forms of heavy metals - DSTU 4770.3: 2007, DSTU 4770.9:2007. The content of heavy metals in the grain - atomic absorption method on a spectrophotometer AAS-3 after the destruction of organic matter with nitric acid and heat treatment (GOST 30178-96). To assess soil contamination, the coefficient of technogenic concentration Kc was used, which characterizes the ratio of the real content of the chemical element in the soil $\underline{Ca}$ to the background content of the same element $\underline{Sf}$ in the environment: $Kc = Ca/Sf$. The value of Kc indicates the activity of the processes of leaching ($Kc < 1$) and accumulation ($Kc > 1$) of chemical elements in the soil (Petruk et al., 2013).

RESULTS

The study of the amount of heavy metals in the soil is important in the study of its nutrient regime. The results obtained in long-term experiments are of great value, as it takes into account the influence of factors provided by fertilizer options. The results of research showed that the systematic use of fertilizers in field crop rotation had an impact on the accumulation of heavy metals in the gray forest soil. According to the results of research it was found

that in the arable (0-20 cm) layer of soil with different fertilizer systems in crop rotation, the content of mobile forms of heavy metals varied within: plumbum 0,50-1,00 mg/kg, cadmium, respectively – 0,07-0,10 mg/kg (Fig. 1 i 2).

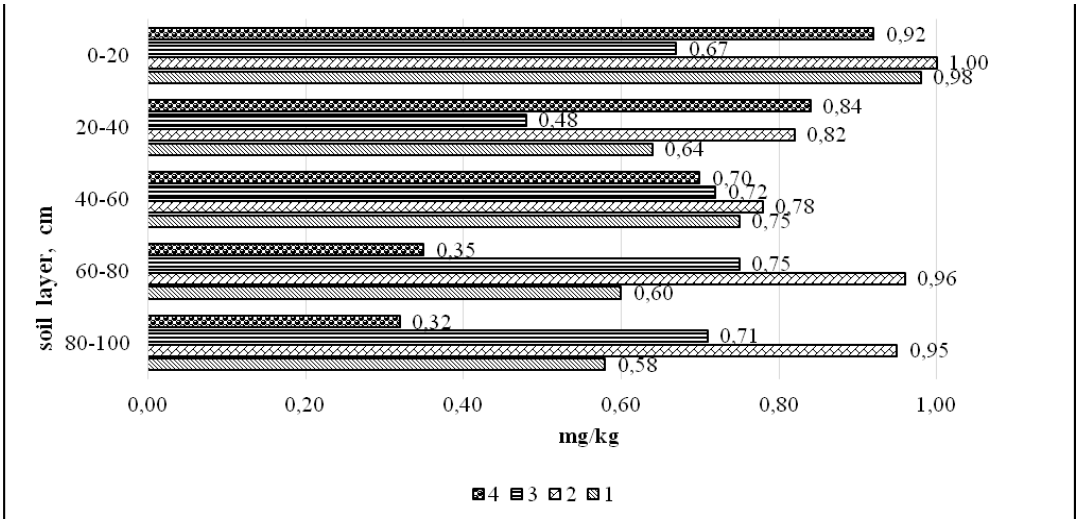

Figure 1. Plumbum content (mg / kg) in gray forest soil under different fertilizer systems, average for 2016-2018.
Notes: The background of the content of mobile forms of plumbum in the gray forest soil, a layer of 0-20 cm is 0.5 mg/kg. Variant: 1 – No fertilizers (control); 2 - 60 t/ha of manure + $N_{100}P_{60}K_{100}$; 3 - 60 t/ha of manure; 4 – $N_{100}P_{60}K_{100}$.

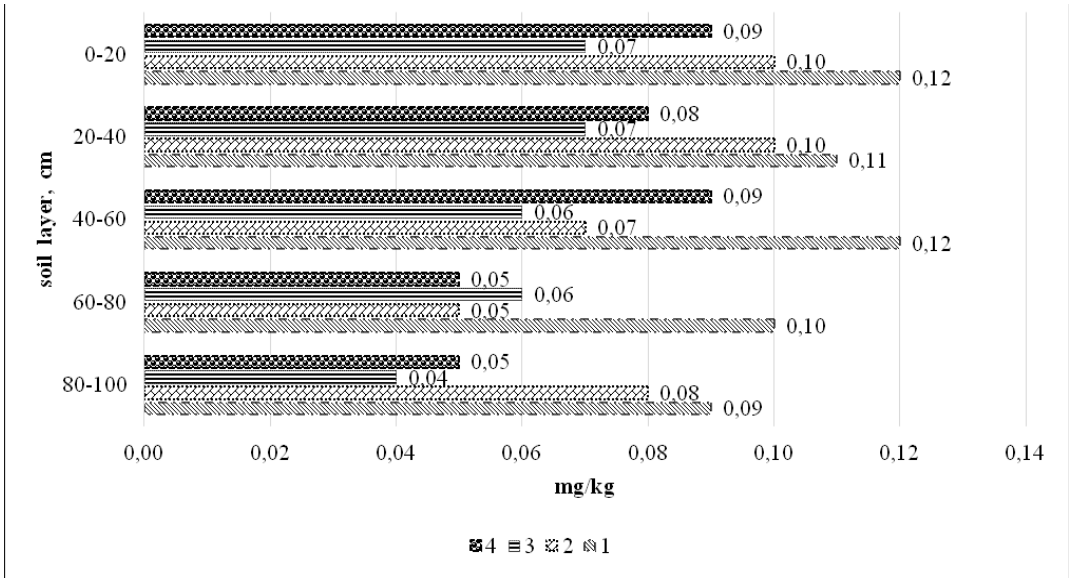

Figure. 2. Cadmium content (mg / kg) in gray forest soil under different fertilization systems, average for 2016-2018.
Notes: Background of the content of mobile forms of plumbum in the gray forest soil, the layer of 0-20 cm is 0,5 mg/kg. Variant: 1 – No fertilizers (control); 2 - 60 t / ha of manure + $N_{100}P_{60}K_{100}$; 3 - 60 t / ha of manure; 4 – $N_{100}P_{60}K_{100}$.

The obtained data on the content of the most available to plants heavy metal compounds, indicate that their content was lower or did not change in all studied variants, compared with the soil before the establishment of a stationary experiment. Regardless of the fertilizer system, there was a tendency to reduce the content of mobile forms of plumbum, mainly in the organic fertilizer system to 33% relative to the initial level. These results are consistent with data from other scientists on the reduction of mobile forms of heavy metals in the topsoil with its intensive use in agriculture (Dmitruk, 2006)**.** This effect is more pronounced with the use of fertilizers, because under these conditions, metals are more actively fixed by organo-mineral compounds, forming less mobile organo-mineral complexes, and are included in plant organisms in the absence of the necessary trace elements.

Studies have shown that the indicator of the coefficient of man-made concentration was Kc> 1, ie there is a process of its accumulation. When calculating the coefficient of contamination by heavy metals, the highest value was observed for plumbum (Kc – 2), cadmium within (Kc – 1). Moreover, the use of organic and mineral fertilizers increased the Kc of plumbum, and organic fertilizers - cadmium, relative to the background level, which indicates the influence of agro-technogenic component in the total man-made pollution (Fig. 3).

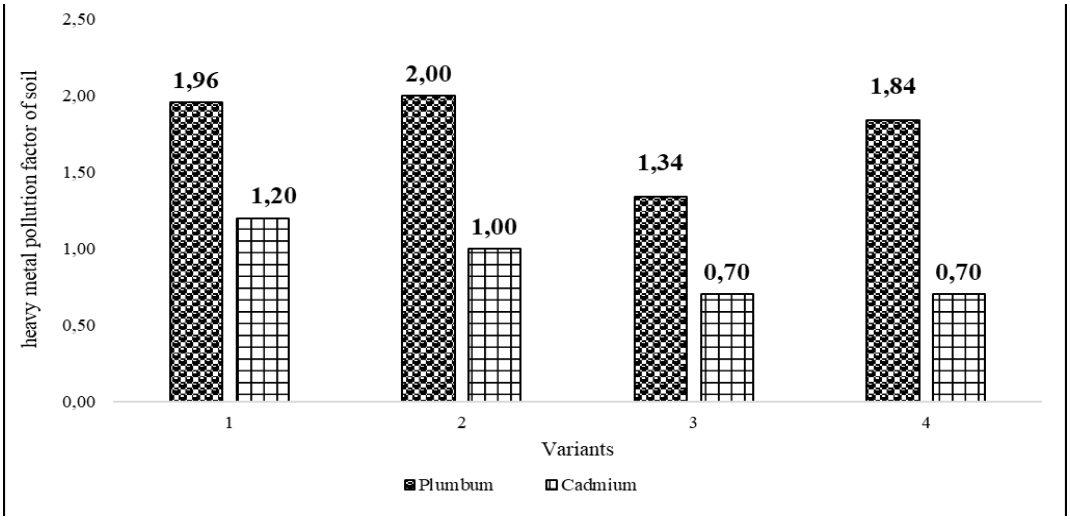

Figure 3. Influence of fertilizer system on the coefficient of technogenic concentration of heavy metals in gray forest soil, layer 0-20 cm, in average from 2016 to 2018.

Notes: Variant. 1 – No fertilizers (control); 2 - 60 t/ha of manure + $N_{100}P_{60}K_{100}$; 3 - 60 t/ha of manure; 4 – $N_{100}P_{60}K_{100}$.

It should be noted that the gray forest soil is characterized by radial migration of low molecular weight organic matter and silty particles, usually rich in heavy metals, with their accumulation in the illuvial horizon of the soil profile. The obtained data on mobile, most accessible to plants heavy metal compounds, indicate that their content was higher or did not change in all variants of the experiment compared to the control variant. These results are consistent with data from other scientists on the increase of mobile forms of heavy metals in the upper layer of the soil with its intensive use in agriculture.

Despite the common opinion about the accumulation of heavy metals only in the upper layer of the soil and the reduction of their reserves with the depth of the profile to the value of the background content of the soil, we found a different trend. Thus, according to the obtained data, the distribution of mobile forms of heavy metals in the soil profile depended on the peculiarities of soil genesis. Under the organo-mineral fertilizer system, there was a tendency to increase reserves in the lower part of the illuvial humus and the upper - illuvial horizons, which within the experimental field formed at a depth of 50-80 cm, as well as a decrease in the humus-eluvial and illuvial humus horizons – 25–45 cm (see Figs. 1 and 2).

The level of heavy metals in the biosphere has increased significantly in recent decades. Today, they are one of the most common pollutants in the agro-ecosystem, which can plumbum to exceeding the limit values of their content in agricultural plants, and thus reduce yields, quality of crop products. (Stepanok, 2001). Contamination of crop

products, on the other hand, is sometimes associated with intensification of agriculture, considering fertilizers a source of exogenous inflow of heavy metals into the agroecosystem (Baranovsky et al., 2006). However, the influence of the fertilizer system in grain row crops on the accumulation of heavy metals by crops remains insufficiently studied.

The study of yield levels shows the systematic use of fertilizers is an indisputable factor in increasing the yield levels of winter wheat. The lowest value is observed at the control (without fertilizers) – 3,06 t/ha. The most effective was the use of organo-mineral fertilizer system $N_{100}P_{60}K_{100}$ + 60 t/ha of manure for an increase of 2,39 t/ha compared to the control, the use of a purely mineral fertilizer system was slightly inferior to the previous level for a decrease of 0,37 t/ha (Table 1).

Table 1. Grain yield of winter wheat under different fertilizer systems in the field experiment, in average from 2016 to 2018

Fertilizer rate per 1 hectare		Yield, t/ha	Increase in control, t/ha	Heavy metal content, mg/kg dry matter	
manure, t*	NPK, kg			plumbum	cadmium
Without fertilizers (control)		3,06	-	0,30	0,0
60	$N_{100}P_{60}K_{100}$	5,45	2,39	0,41	0,0
60	$N_0P_0K_0$	4,53	1,47	0,30	0,0
-	$N_{100}P_{60}K_{100}$	5,08	2,02	0,36	0,0
SSD $_{05}$		0,15		0,10	0,0
MPC				0,50	0,1

* *Notes:* IV year after litter manure

Studies of the content of heavy metals in the main products of winter wheat show the stability of levels of contamination by these elements of grain within acceptable concentrations of MPC up to 0,5 mg/kg, but with systematic application of mineral fertilizers at elevated rates can eventually be dangerous.

CONCLUSIONS

- ✓ It was found that the content of mobile forms of heavy metals was lower or did not change in all studied variants compared to the initial content, but regardless of the fertilizer system there was a tendency to reduce the content of mobile forms of plumbum, mainly in organic fertilizer system to 33% relative to baseline.
- ✓ It was found that the highest level of man-made concentration coefficient for plumbum (Kc = 2) was obtained by organo-mineral fertilizer system ($N_{100}P_{60}K_{100}$ on the background of 60 t/ha of manure), cadmium within (Kc = 1), with the use of organic fertilizers (60 t/ha of manure).
- ✓ It was determined that the distribution of mobile forms of heavy metals according to the soil profile depended on the peculiarities of soil genesis and fertilizer system. Thus, there was a tendency to increase the content of mobile forms of lead and cadmium agrochemical load in the norm $N_{100}P_{60}K_{100}$ on the background of 60 t / ha of manure, in the lower part of illuvial humus and upper - illuvial horizons formed within the experimental field at a depth of 50-80 cm, and decrease at the boundary of humus-eluvial and illuvial humus horizons – 25–45 cm.
- ✓ It was found that the highest level of yield provides the use of organo-mineral fertilizer system $N_{100}P_{60}K_{100}$ + 60 t/ha of manure for an increase of 2,39 t/ha compared to control, the use of purely mineral fertilizer system was slightly inferior to the previous level for a decrease of 0,37 t/ha. Studies of the content of heavy metals in the main products of winter wheat indicate the stability of levels of contamination by these elements of the grain within the permissible concentrations of MPC.

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