Environ Geochem Health (2023) 45:85–100
https://doi.org/10.1007/s10653-021-01193-6

ORIGINAL PAPER

The effect of resource-saving tillage technologies on the mobility, distribution and migration of trace elements in soil

Anna M. Medvedeva · **Olga A. Biryukova** · **Alexey V. Kucherenko** ·
Yaroslav I. Ilchenko · **Tatiana M. Minkina** · **Saglara S. Mandzhieva** ·
Mahmoud Mazarji

Received: 27 February 2021 / Accepted: 23 December 2021

Abstract The influence of agricultural tillage technologies on the accumulation and distribution of trace elements in the soil is poorly studied. At the same time, intensive agriculture requires large amounts of fertilizers, growth stimulators, pesticides, and other substances, which can effect the ecological safety of the plant products and soil. This paper represents studying the effect of various agricultural techniques (including resource-saving technologies) on the mobility and profile distribution of Pb, Zn, and Cu in Haplic Chernozem. No significant influence of resource-saving tillage technologies was found on the total Pb content. Contrary, the resource-saving tillage technologies was observed to promote the growth of the total Zn and Cu content depending on the cultivation method (by 26% Zn, 34% Cu at minimal tillage, and 28% for both elements using No-till in Ap horizon). Amongst different applied agrotechnologies, there was no influence found on the profile distribution of total elements content. Only two horizons showed the total Pb content accumulation: biogenic (Ap-A) and carbonate (BC-C) horizon. In contrast, the only biogenic accumulation for Zn was determined. Copper characterizes by even distribution over the soil profile. The use of resource-saving agricultural technologies increases exchangeable fraction of Zn, Pb and Cu in soil almost by 1.5–2.0 times in the Ap horizon compared to moldboard ploughing. Despite the increase in the exchangeable fraction of Zn and Cu, this amount of micronutrients is not enough for adequate plant nutrition. The use of various agricultural technologies at Haplic Chernozem led to changes in the distribution of studied elements' exchangeable fraction over the soil profile. The study results suggested a need to increase the amount of Cu and Zn fertilizers applied to the soil with resource-saving cultivation technologies.

Keywords Soil cultivation · Copper · Zinc · Lead · Microelements · No-till

Introduction

Maintenance and recovery of soil fertility are the main condition for the sustainable development of agriculture. Mechanical soil cultivation systems and fertilizers are some of the main parts of modern agriculture (Franzluebbers, 2004; Malhi et al., 2018). Traditional tillage technology using moldboard ploughing is the most common method of soil cultivation with some disadvantages. In some cases, the impact of tillage

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A. M. Medvedeva (✉) · O. A. Biryukova ·
A. V. Kucherenko · Y. I. Ilchenko ·
T. M. Minkina · S. S. Mandzhieva · M. Mazarji
Academy of Biology and Biotechnology, Southern
Federal University, 194/1 Prosp. Stachki Ave.,
Rostov-on-Don, Russian Federation 344090
e-mail: medvedeva.estelior@yandex.ru

tools could lead to a decrease in soil quality and fertility and even to its degradation (Herrera et al., 2020; Montgomery, 2007). Implementing of resource-saving cultivation technologies has a positive outcome on some soil properties, supports the formation of the natural soil structure, and improves the crop yield by maintaining the soil's natural fertility (Acar et al., 2018; Malhi et al., 2018).

Very few studies are currently devoted to analyzing the influence of agricultural tillage technologies on the accumulation and distribution of trace elements in the soil (Moreira et al., 2019; Smurov et al., 2014). However, resource-saving tillage technologies have a significant disadvantage due to the requirements of high doses of mineral fertilizers, crop protection products, growth stimulators, and structuring agents that may contain potentially toxic elements (Muchuweti et al., 2006). Moreover, the applied chemicals remain mostly in the upper soil layer, leading to the accumulation of potentially toxic elements by crops, thus impacting product safety and human health (Wuana & Okieimen, 2011). Considering the significant number of users of resource-saving agricultural tillage technologies globally, the influence of these technologies on the accumulation and distribution of trace elements in the soil is of great importance to study.

The low quality of crop products can be associated with highly hazardous substances and insufficient multi-element crop nutrition (Paul et al., 2014). The bioavailability of Pb, Cu and Zn depend on its chemical form in soil (Li et al., 2016; Martınez & Motto, 2000; Raskin & Ensley, 2000). At the same time, the low content of exchangeable fraction of trace elements is one of the negative factors affecting the yield and quality of agricultural products (Biryukova et al., 2015). In this context, the soil's low background content and the negative balance of many trace elements in agrocenosises are caused by an insufficient fertilizer (Kumar et al., 2016). The use of resource-saving agricultural technologies requires additional micronutrients in soils related to their high consumption by crops and intensive agriculture (Kachinski et al., 2020). The lack or excess of an element on the crop quality also depends on the biological role of this element.

The biological role of Pb is poorly studied in contrast to Zn and Cu, which are involved in many physiological and biochemical processes. The low content of Pb in the soil can positively affect the growth and development of plants (Kabata-Pendias, 2010). Contrary, the high amount of Pb in soil negatively affects seed germination, plant growth, root system development, cell division, the intensity of transpiration and photosynthesis, and eventually resulting in Pb accumulation in the plants (Figlioli et al., 2019; Silva et al., 2017). Therefore, Cu and Zn were selected as they are essential micronutrients for the plants, while the Pb selection was based on being a potential pollutant.

The purpose of our study is to assess the impact of traditional and resource-saving tillage technologies on the total content and exchangeable fractions of Zn, Cu, and Pb in Haplic Chernozem. To fulfill the goal, we conducted long-term monitoring of the content, distribution, and migration on the profile of these elements under the use of various agrotechnologies.

Materials and methods

Description of research site and experimental design

Meteorological data

The studied area is located in the Lower Don River (Rostov oblast, Russia). The climate in the study area is sharply continental and dry. Winter is moderately mild, and summer is relatively dry, with the highest temperatures in June or August. Dust storms and dry winds are observed several days a year. The average annual air temperature for 2014–2020 was above the norm and ranged from 10.1 to 10.8 °C with moderately hot summers, droughts, and relatively warm autumn. The warmest year was 2019, which was characterized by a short winter. For the period 2015–2020 in the study area, precipitation was 452–594 mm. On average, the smallest amount of precipitation in the region fell in 2015–452 mm (92% of the norm), the highest in 2016–594 mm (121% of the norm). Precipitation was close to normal in 2017 and 2018.

Description of applied agricultural technologies

In this research, we studied three agricultural technologies: moldboard ploughing (ploughing to a depth of 25–27 cm, lift-type disc plough 4–35), direct seeding (no-till) (Semeato TDNG - 420, Brazil), and minimal tillage at the depth 10–12 cm (heavy disk harrow - 3). The never-tilled soil (virgin site) was used as a control.

The main difference between the studied technologies is the soil tillage techniques that determined the method of fertilization with ammonium dihydrogen phosphate (ADP) ($NH_4H_2PO_4$, 12% N and 52% P_2O_5) at a dose of 100 kg ha^{-1}. Ammonium dihydrogen phosphate was applied under plowing with seam turn in moldboard ploughing, using minimal technology—in pre-sowing cultivation, and with no-till during winter wheat sowing. The rest of the fertilizer elements and crop protection systems were similar. During the vegetation season of winter wheat, ammonium nitrate (NH_4NO_3, 34% N) was used in autumn in the tillering phase (100 kg ha^{-1}). In the spring with vegetation renewal, 10-% carbamide solution ($CO(NH_2)_2$, 46% N, 200 kg ha^{-1}) was used for foliar fertilizing of the plants (at the beginning of stem extension phase). Potash fertilizers were not used since the farm soils were characterized by an enough amount of available potassium (463 mg kg^{-1}). If necessary, herbicides and insecticides were applied in the tillering phase and after the flank leaf development. The cultivated crop was winter wheat (*Triticum aestivum* L.).

Soil sampling

The soil samples were collected annually from 2014 until 2020 during the spring–summer period on the agricultural farm territory, which has been used for various agricultural technologies, including resource-saving (Fig. 1). The minimal tillage technology on the farm's territory has been used since 2000, and no-till technology (direct sowing) since 2008.

According to the World Reference Base (WRB), the soil is characterized as Haplic Chernozem (IUSS Working Group WRB 2015).

A total of 95 soil samples were collected during the study. The depth of the horizons was different in areas with different agrotechnologies and in the never-tilled soil, i.e., virgin land. For never-tilled soil, in averages for the horizon it was Ap (0–10 cm), A (11–52 cm), AB (54–73 cm), Bca (74–99 cm), BC (100–110 cm), C (110–130 cm); for no-till Ap (0–6 cm), A (7–39 cm), AB (40–73 cm), Bca (74–99 cm), BC (100–125 cm), C (126–135 cm); for minimal tillage Ap (0–10 cm), A (11–42 cm), AB (43–60 cm), Bca (61–106 cm), BC (107–124 cm), C (125–135 cm); for moldboard ploughing Ap (0–25 cm), A (26–42 cm), AB (43–71 cm), Bca (72–90 cm), BC (91–126 cm), C (127–145 cm). Soil sampling was carried out from the middle of the soil horizon according to GOST 28168-89 (1989).

The soil samples were dried at room temperature, ground, and sieved (1 mm mesh) to remove residuals, such as visible stones and plants, and stored at 4 °C until further use.

Soil sample analysis

The following methods determined the main physicochemical properties of the soils presented in Table 1: the soil organic carbon (Corg) content, by titrimetry using wet combustion (dichromate oxidation) procedure (Vorob'eva 2006); total N content by Kjeldahl's method (GOST 26107-84); total P content by X-ray fluorescent (XRF) scanning spectrometer SPECTROSCAN MAX-GV (Vorob'eva 2006); the content of exchangeable P and available K by Machigin's method (Vorob'eva 2006); the content of $CaCO_3$, by Kudrin's method (Vorob'eva 2006); the exchangeable Ca^{2+} and Mg^{2+}, by the method of Shaimukhametov (Shaimukhametov, 1993); the soil particle size distribution, by the pipette method with pyrophosphate pretreatment (Vadyunina & Korchagina, 1986), and the pH of soil water suspension (soil to water ratio 1: 2.5), by potentiometry.

The total Cu, Zn, and Pb content in the soil was determined by XRF spectrometer SPECTROSCAN MAX-GV ("SPECTRON", Ltd., Russia). All samples were analyzed using the bulk mode for soil sample. Each sample was analyzed for 45 s (PND F 16.1.42-04).

The exchangeable fractions of metals were extracted with 1 M CH_3COONH_4 (pH 4.8), the ratio of soil to the solution was 1: 10 (Minkina et al., 2018). Briefly, the suspensions were shaken for an hour and then left for 18 h, after which they were filtered. The concentration of extracted elements was determined by atomic absorption spectrometry (AAS) with electrothermic atomization and polarization Zeeman effect correction for nonselective adsorption using an MGA-915MD spectrometer (Lumex Scientific-Production Company, St. Petersburg, Russia).

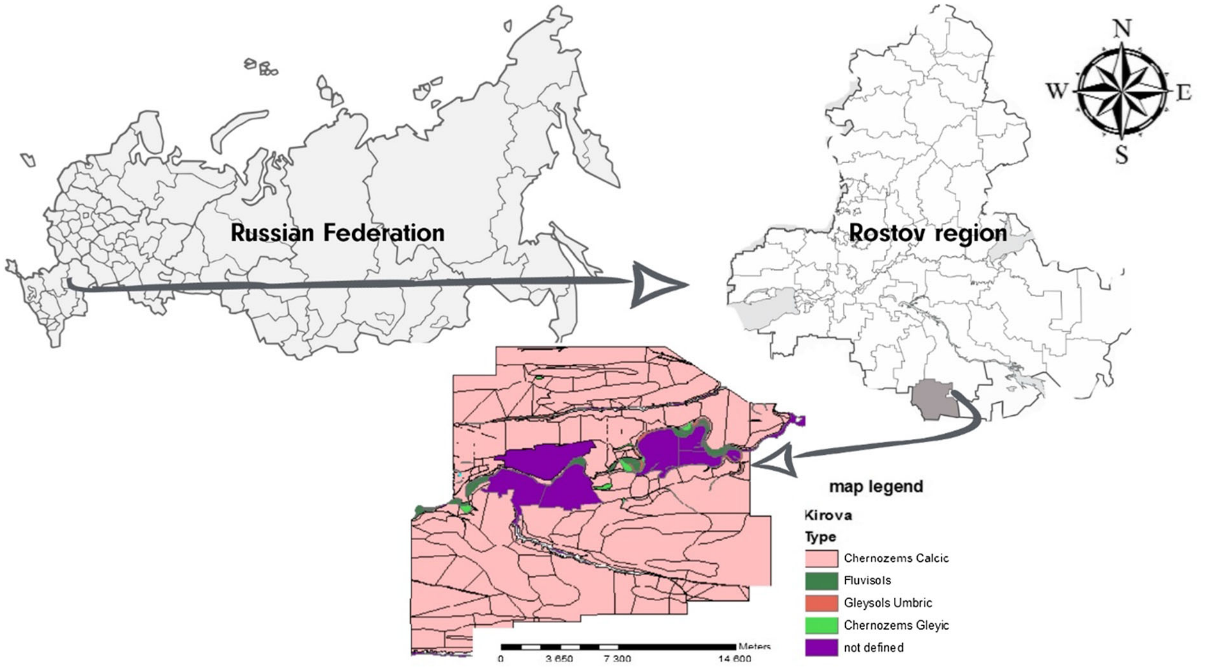

Fig. 1 Map of the research region

Table 1 Physicochemical properties of the studied soil. Parameters are presented for the never-tilled soil

Horizons	Organic carbon (Corg), g kg^{-1}	Total nitrogen, g kg^{-1}	Total phosphorus, g kg^{-1}	Exchangable phosphorus, mg kg^{-1}	Available potassium, mg kg^{-1}	Exchangeable cations $Ca^{2+} + Mg^{2+}$, cmol kg $^{-1}$
Ap(0-10 cm)	48.6–53.3	2.8–3.1	1.8–1.9	16.2–24.1	464–532	328–339
A(11-52 cm)	34.1–35.2	2.3–2.6	1.5–1.6	15.6–21.3	443–524	324–330
AB(53-73 cm)	29.3–29.6	1.8–2.3	1.5–1.6	13.8–17.4	324–376	320–330
Bca(74-99 cm)	20.5–24.1	1.4–2.0	1.4–1.5	13.4–17.6	195–217	326–328
BC(100-110 cm)	14.5–20.4	1.1–1.6	1.3–1.5	12.8–18.0	178–196	320–324
C(111-130 cm)	6.3–8.6	1.3–1.5	1.4–1.5	14.4–14.6	160–172	310–316

Horizons	$CaCO_3$, g kg^{-1}	pH	Particles < 0.01 mm, g kg^{-1}	Particles < 0.001 mm, g kg^{-1}
Ap(0-10 cm)	16–18	7.9–8.2	467.8–516.9	211.6–248.0
A(11-52 cm)	23–26	8.0–8.2	483.1–499.2	181.8–270.3
AB(53-73 cm)	54–58	8.0–8.2	498.9–613.0	153.7–230.0
Bca(74-99 cm)	79–86	8.0–8.2	494.9–564.7	224.4–304.0
BC(100-110 cm)	121–123	8.1–8.3	490.3–623.9	179.5–316.3
C(111-130 cm)	158–162	8.2–8.4	484.8–569.7	177.3–284.8

All the analysis were performed in triplicate.

Assessment of elements migration in the soil profile

The accumulation coefficient was calculated to analyze the influence of agricultural technologies on the accumulation and removal of trace elements according to the following equation (Gavrilyuk, 1955).

$$K = C_{\mathrm{Ap}}/C_{\mathrm{C}}, \quad (1)$$

where C_{Ap} is the content of the particular element in the surface horizon, and C_{C} is the content of the metal in the C horizon.

If $K > 1$, the element is accumulated in the surface layer of soil, and the value of $K < 1$ indicates that the chemical element is leached from the surface layer to the lower layers of the soil (Gavrilyuk, 1955).

The obtained values were compared to the existing standards for the determination of maximum permissible concentration (MPC) and approximate permissible concentration (APC) values (Artyushin et al., 1992; Rusakov et al., 2009).

Statistical analyses

Mathematical processing of the results was carried out using correlation and variance analyses (ANOVA) with the STATISTICA software package v. 10-13. The means of treatment, standard mean error, and variation coefficient were also reported at the significance level $p < 0.05$.

Results and discussion

Total content of trace elements

The certain character of the distribution of the trace elements along the profile of Haplic Chernozem was noted for all studied agricultural technologies and in the never-tilled soil (Table 2). For each element, this distribution had a similar character, regardless of the applied agricultural technology. Differences in the distribution of the total content of Pb, Zn, and Cu were occurred due to elements' characteristics and their association with the physicochemical properties of the soil. The total content in the upper humus horizon (Ap/Ad) of Haplic Chernozem varied with all studied agrotechnologies within 70.4–88.8 mg kg^{-1} for Zn, 41.3–55.4 mg kg^{-1} for Cu and 26.4–32.2 mg kg^{-1} for Pb (Table 2). This content of elements corresponds to the background content of metals in the studied region soils (Minkina et al., 2008). The obtained values did not exceed the APC levels under all soil cultivation methods.

For the total content of Cu, the profile was undifferentiated, without clear expressed barriers (Table 2). The biogenic barrier is more expressed for Zn with its accumulation in the Ap–AB horizons (86.2–88.8 mg kg^{-1}). Two biogeochemical barriers are clearly expressed for Pb: biogenic (Ap-A horizon) and carbonate (BC-C horizon) with Pb accumulation.

Zinc, Cu, and Pb have different affinities to the sorption sites of the organic and mineral soil phases and show different availability, mobility, and toxicity (Burachevskaya et al., 2019; Chang et al., 2020; Minkina et al., 2018; Nevidomskaya et al., 2016; Ren et al., 2017). This may explain the different profile distribution of elements in the soil profile. The total content of Zn is characterized by the accumulative type of profile distribution and the accumulation in the upper soil horizons (Ap + AB). The accumulation of Zn in surface horizons may also occur due to the adsorption of the element by SOM.

The total content of Pb is characterized by the maximum accumulation of an element in the upper layer and lower horizons (Table 2). The organophilicity of Pb is well known (Kabata-Pendias, 2010). Moreover, Pb is characterized by a high ability to form a strong stable complex with SOM (Bauer et al., 2015). Haplic Chernozem is formed in conditions of a nonpercolative regime and has a high amount of highly dispersed form of carbonates (Table 1). The role of these forms of carbonates in the migration and adsorption of trace elements is important in Haplic Chernozems of the Lower Don River region (Minkina et al., 2008).

Statistical analysis showed the relative stability of distribution of the total content of Cu and Zn in soil profile both in the never-tilled soil and after the implementation of the studied agricultural technologies (Table 2). The coefficient of variation for both elements in soil horizons with all studied agrotechnologies was below or equal to 10%, except the Cu content in Ap horizon with minimal soil tillage (13%). The total content of Pb was more varied and was more expressed in the never-tilled soil profile and with

Table 2 The total content of trace elements in the profile of Haplic Chernozem using various agricultural technologies, $n = 95$

Horizon	Total content of Pb, mg kg^{-1}		Total content of Cu, mg kg^{-1}		Total content of Zn, mg kg^{-1}	
	M ± m	*V*, %	M ± m	*V*, %	M ± m	*V*, %
No-till						
Ap	26.86 ± 2.22	17	52.81 ± 0.89	3	88.76 ± 2.86	6
A	25.63 ± 1.25	10	53.81 ± 0.57	2	89.03 ± 3.36	8
AB	16.79 ± 0.13	2	56.15 ± 1.71	6	85.31 ± 2.79	7
Bca	17.82 ± 0.82	9	54.21 ± 1.33	5	83.41 ± 2.47	6
BC	24.31 ± 1.42*	12	53.34 ± 2.43	9	81.47 ± 2.16	5
C	30.05 ± 0.53	4	54.02 ± 2.20	8	82.26 ± 1.93	5
Minimal tillage						
Ap	32.21 ± 2.44	15	55.41 ± 3.54	13	88.43 ± 0.74	2
A	23.75 ± 0.58	5	54.11 ± 2.27	8	86.16 ± 2.44	6
AB	18.17 ± 1.32	15	56.44 ± 1.38	5	86.99 ± 1.94	4
Bca	18.75 ± 1.75	19	55.73 ± 1.69	6	86.44 ± 0.68	2
BC	28.98 ± 2.89	20	54.34 ± 2.53	9	85.11 ± 1.84	4
C	29.11 ± 3.43	20	56.80 ± 0.38	1	82.50 ± 0.08	0
Moldboard ploughing						
Ap	26.36 ± 1.21	9	41.27 ± 1.07*;**;***	5	70.39 ± 1.53*,**,***	4
A	27.93 ± 0.94***	6	41.20 ± 1.53*,**,***	7	70.53 ± 1.18*,**,***	3
AB	14.97 ± 0.83	11	48.83 ± 0.91*,**,***	4	72.07 ± 0.89*,**,***	2
Bca	17.02 ± 0.75	9	43.67 ± 1.21*,**,***	6	62.27 ± 1.21*,**,***	4
BC	21.39 ± 1.09***	10	39.79 ± 1.32*,**,***	7	64.58 ± 1.11*,**,***	3
C	19.80 ± 0.89*,**,***	9	41.46 ± 0.68*,**,***	3	62.79 ± 0.91*,**,***	3
Never-tilled soil						
Ap	28.01 ± 1.13	8	50.22 ± 2.62	10	84.56 ± 3.03	7
A	26.12 ± 1.11	8	53.33 ± 1.26	5	83.66 ± 1.68	4
AB	16.98 ± 2.67	31	53.33 ± 1.21	5	86.52 ± 1.81	4
Bca	15.13 ± 1.94	26	53.09 ± 1.21	5	83.92 ± 1.76	4
BC	18.28 ± 1.72	19	52.78 ± 2.13	8	83.79 ± 1.40	3
C	30.11 ± 1.05	7	49.18 ± 2.50	10	78.99 ± 1.46	4
APC, mg kg^{-1}	130		132		230	

M—mean value; m—mean error; V—variation coefficient

*significant statistical difference of element content in the horizon between studied agrotechnologies and never-tilled soil; **significant statistical difference of element content in the horizon between studied agrotechnologies and no-till; ***significant statistical difference of element content in the horizon between studied agrotechnologies and minimal tillage

minimal tillage (15 – 31%). Such variability can be explained by the accumulation of SOM (Medvedeva et al., 2021), the migration of carbonates along with the profile of Chernozem (Table 1, Fig. 2), and the presence of alluvial processes. The content of carbonates in profile with studied agrotechnologies decreased in comparison with never-tilled soil. This indicates a slight change in the content of carbonates with prolonged agricultural use of soil.

The introduction of resource-saving technologies compared to moldboard ploughing did not affect the content of total Pb in soil (Fig. 3a). However, it caused a significant increase in the content of Cu and Zn in the profile of Haplic Chernozem (Fig. 3b and c). This could be explained as a result of using resource-saving

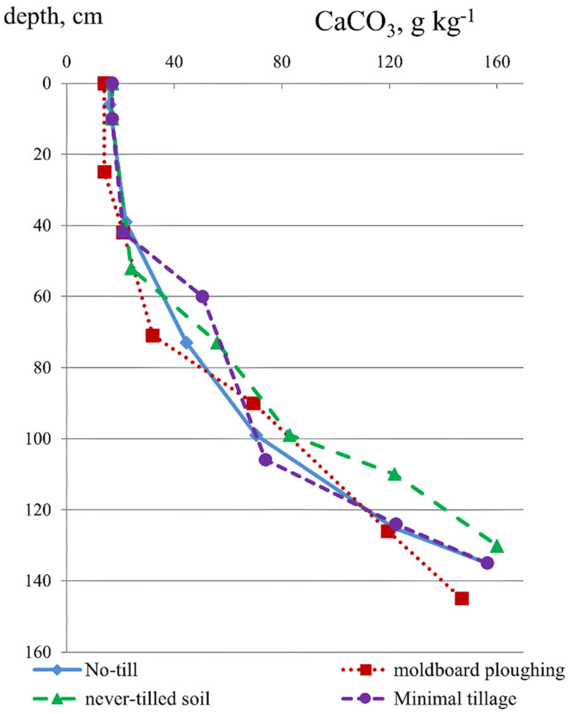

Fig. 2 The profile distribution of carbonates content in Haplic Chernozem with different tillage technologies

agrotechnologies for 20 years. This pattern is a consequence of the continuous adding of high doses of fertilizers and crop protection products. Also, an increase in the total Zn and Cu concentration in the soil may be due to their input into the soil with the mineralization of the plant mass, accumulating in the upper soil horizon during the application of resource-saving agrotechnologies. Horizon Ap was characterized by the rise of Zn by 26% for both resource-saving technologies, by 34% for Cu during minimal tillage, and by 28% during no-till compared to moldboard ploughing.

Exchangeable fraction of trace elements

The distribution of the exchangeable fraction of Pb, Cu, and Zn was studied within the vertical profile of the Haplic Chernozem using various agricultural technologies is shown in Table 3. The content of exchangeable fractions of Pb, Cu, and Zn showed more reliable information on the content and effect of trace elements on the ecological status of agrocenosises. The content of Zn, Pb and Cu exchangeable fractions did not exceed the MPC levels under all soil cultivation methods; thus, these elements could not accumulate in agricultural plants (Table 3).

In general, Pb distribution corresponded to the eluvial type of distribution with minimum content in the upper layer and maximum in the middle and lower layers of the profile. However, a comparison of the soil profile using various agricultural technologies showed some differences. In this context, the distribution of Pb in profiles of the never-tilled and soil using no-till technology can be attributed to the progressive-eluvial-illuvial type (with the accumulation of the element in the upper and lower layers). The use of moldboard ploughing and the minimal tillage slightly change the profile distribution of Pb to the eluvial-illuvial type (with a minimum content in the upper layer and a maximum in middle or lower layers). These differences can be explained by the more intensive accumulation of SOM in the never-tilled soil and no-till implementation. This contributes to a more intensive fixation of Pb in organic horizons than with ploughing and minimal tillage, suggesting subtype differences of the profile distribution of the element. The important role of the soil reaction pH in the retention of Pb in the soil is known (Yong et al., 2015). At neutral pH, 90% of Pb exists in organic complexes. At an alkaline pH, Pb mainly exists in Pb carbonates and phosphates, which are insoluble and unavailable for plants (Mahar et al., 2018). The slightly alkaline pH level (Table 1) is also typical for the studied soil, which probably was the reason for the formation of Pb carbonates and phosphates.

A uniformly eluvial profile was observed for the exchangeable fraction of Cu, with a gradual increase of its content moving to the underlying layers. Copper is represented in soil by several forms associated with different components of soil. The character of these associations affects mobility and the presence of this element (Dong and Wang 2012). A slightly higher content of exchangeable fraction of Cu (0.14–0.24 mg kg^{-1}) was observed in the carbonate horizon (Bca). As a result of interaction with carbonates, Cu was in the soil (Table 3). Similar results were obtained in the Voronezh region on Typical and Haplic Chernozems (Protasova et al., 2015).

In the never-tilled soil, the profile distribution of Zn corresponded to the accumulative type with the maximum of the element in the surface layer (0.37 mg kg^{-1}) and a gradual decrease by depth (0.24 mg kg^{-1}). The mobility of Zn in Haplic

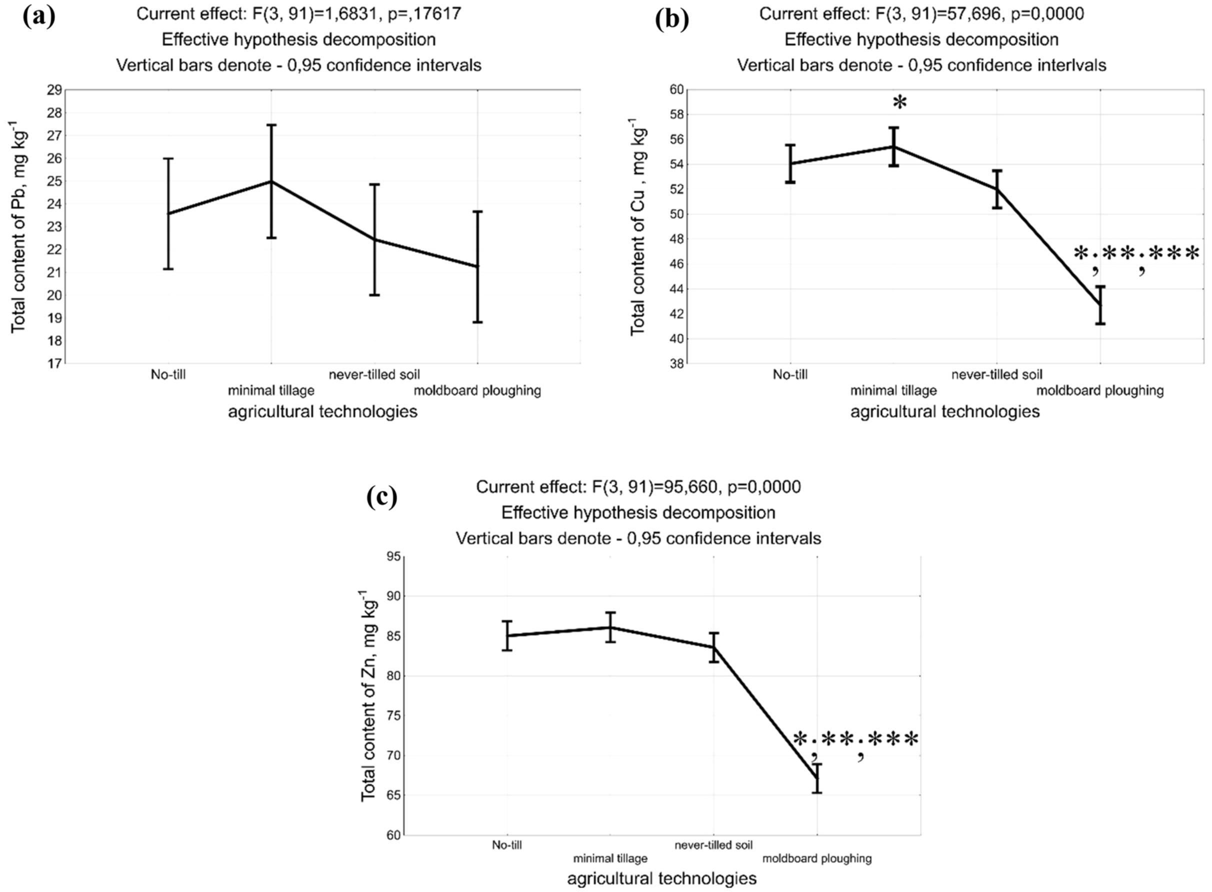

Fig. 3 Influence of agricultural technologies on the total content of **a** Pb, **b** Cu and **c** Zn in Haplic Chernozem (*significant statistical difference of element content between studied agrotechnologies and never-tilled soil; **significant statistical difference of element content between studied agrotechnologies and no-till; ***significant statistical difference of element content between studied agrotechnologies and minimal tillage)

Chernozem is very low and decreases with the depth related to the alkalization of the medium (Fonseca et al., 2010; Minkina et al., 2008). Agricultural use of Haplic Chernozem leads to a change in the profile distribution of Zn. Eluvial-illuvial type of profile was found in all studied cultivations (Table 3).

A higher coefficient of variation of almost all elements was observed in the profiles using minimal tillage and no-till technology (Table 3). The maximum variation of 23–39% and 28–43% was found for Pb using no-till and minimal tillage, respectively, and Pb was accumulated in the upper organic horizons Ap − AB. Variation of Zn content in the soil profiles with resource-saving tillage reached a maximum in the Bca horizon. This element was almost stable within the entire profile using moldboard ploughing and in the never-tilled soil.

According to the obtained results, Haplic Chernozem is characterized by a low content of exchangeable fraction of Zn (< 2.0 mg kg^{-1}) and Cu (< 0.2 mg kg^{-1}) that probably occurred due to the active absorption of these elements by plants and insufficient use of Zn- and Cu-containing fertilizers (Table 3). The low content of these elements was noted for all the studied agricultural technologies and in the never-tilled soil. Reducing the elements content of exchangeable fraction may also depend on the SOM content, soluble forms of phosphates, the content and migration of carbonates, a weakly alkaline reaction of the environment, and a heavy-loamy texture (Konstantinova et al., 2021; Kumar et al., 2016; Vodyanitskii et al., 2021).

The obtained results have shown that introducing resource-saving technologies increased the

Table 3 The content of exchangeable fraction of trace elements within the profile of Haplic Chernozem using various agricultural techniques, $n = 95$

Horizon	Exchangeable fraction of Pb, mg kg^{-1}			Exchangeable fraction of Cu, mg kg^{-1}			Exchangeable fraction of Zn, mg kg^{-1}		
	M ± m	*V*, %	% of exchangeable fraction of Pb of total Pb content	M ± m	*V*, %	% of exchangeable fraction of Cu of total Cu content	M ± m	*V*, %	% of exchangeable fraction of Zn of total content Zn
No-till									
Ap	0.75 ± 0.15	39	2.9	0.12 ± 0.01	19	0.2	0.55 ± 0.08	30	0.6
A	0.79 ± 0.15	38	3.0	0.14 ± 0.03	45	0.3	0.42 ± 0.07	34	0.5
AB	0.59 ± 0.07	23	3.6	0.16 ± 0.02	21	0.3	0.32 ± 0.05	34	0.4
Bca	0.55 ± 0.03	12	3.1	0.19 ± 0.03	29	0.4	0.46 ± 0.11	50	0.5
BC	0.71 ± 0.07	21	2.9	0.28 ± 0.02	12	0.5	0.33 ± 0.05	32	0.4
C	0.69 ± 0.07	21	2.3	0.29 ± 0.01	7	0.5	0.31 ± 0.03	21	0.4
Minimal tillage									
Ap	0.60 ± 0.12	39	1.9	0.12 ± 0.01	21	0.2	0.53 ± 0.03*	13	0.6
A	0.56 ± 0.08	28	2.4	0.13 ± 0.01	9	0.2	0.34 ± 0.04	23	0.4
AB	0.52 ± 0.11	43	2.9	0.14 ± 0.01	18	0.3	0.59 ± 0.10*	36	0.7
Bca	0.69 ± 0.12	35	3.9	0.19 ± 0.03	35	0.3	0.49 ± 0.15	60	0.6
BC	0.77 ± 0.11	27	2.8	0.27 ± 0.02	18	0.5	0.58 ± 0.12	42	0.7
C	0.88 ± 0.18	36	3.2	0.33 ± 0.06	29	0.5	0.61 ± 0.14**	40	0.7
Moldboard ploughing									
Ap	0.40 ± 0.02*	9	1.5	0.06 ± 0.007**,***	25	0.1	0.27 ± 0.014*,**,***	10	0.4
A	0.46 ± 0.01*	6	1.6	0.04 ± 0.004*,**,***	20	0.1	0.24 ± 0.01*	11	0.3
AB	0.43 ± 0.02*	10	2.9	0.04 ± 0.008*,**,***	37	0.1	0.22 ± 0.009*,***	9	0.3
Bca	0.49 ± 0.02	7	2.9	0.14 ± 0.01*	16	0.3	0.31 ± 0.01*	9	0.5
BC	0.58 ± 0.01	4	2.7	0.18 ± 0.01*,**,***	16	0.5	0.39 ± 0.01*	7	0.6
C	0.64 ± 0.02	7	3.3	0.25 ± 0.01	9	0.5	0.36 ± 0.01*,**,***	6	0.6
Never-tilled soil									
Ap	0.75 ± 0.04	9	2.7	0.08 ± 0.01	30	0.2	0.37 ± 0.01	7	0.4
A	0.59 ± 0.02	6	2.3	0.14 ± 0.01	20	0.3	0.33 ± 0.01	8	0.4
AB	0.54 ± 0.03	10	3.6	0.17 ± 0.01	16	0.3	0.30 ± 0.02	16	0.3
Bca	0.54 ± 0.04	14	3.7	0.24 ± 0.008	7	0.4	0.27 ± 0.01	8	0.3
BC	0.61 ± 0.02	8	3.4	0.25 ± 0.01	10	0.5	0.25 ± 0.02	13	0.3
C	0.63 ± 0.02	6	2.1	0.27 ± 0.01	11	0.6	0.24 ± 0.01	9	0.3

Table 3 continued

Horizon	Exchangeable fraction of Pb, mg kg^{-1}			Exchangeable fraction of Cu, mg kg^{-1}			Exchangeable fraction of Zn, mg kg^{-1}		
	M ± m	*V*, %	% of exchangeable fraction of Pb of total Pb content	M ± m	*V*, %	% of exchangeable fraction of Cu of total Cu content	M ± m	*V*, %	% of exchangeable fraction of Zn of total content Zn
MPC, mg kg^{-1}	6			3			23		

Note: M—mean value; m—mean error; V—variation coefficient. *—significant statistical difference of element content in the horizon between studied agrotechnologies and never-tilled soil; **—significant statistical difference of element content in the horizon between studied agrotechnologies and no-till; ***—significant statistical difference of element content in the horizon between studied agrotechnologies and minimal tillage exchangeable fraction of Cu and Zn in the upper soil horizon compared to moldboard ploughing (Table 3). With minimal tillage and no-till technique, the part of exchangeable Cu in the Ap horizon was 0.2%, and part of Zn was 0.6%. However, these values were 0.1 and 0.4%, after moldboard ploughing, for Cu and Zn respectively. The long-term use of minimal tillage after moldboard ploughing increased the mobility of Zn within the entire profile. Application of no-till increased the exchangeable fraction of Cu and Zn until the carbonate horizon. Further, Cu's mobility difference between tillage methods decreased from the Bca horizon and remains unchanged (0.5%) in the C horizon. At the same time, the exchangeable fraction of Zn in the BC–C horizons was higher during moldboard ploughing. A similar trend was found for Pb. The exchangeable fraction of Pb was also higher than at moldboard ploughing in C horizon using resource-saving tillage methods.

Variance analyses (ANOVA) of the data showed a statistically significant effect of the tillage method on the exchangeable fraction of Pb, Zn, and Cu (Fig. 4). The content of the exchangeable fraction of all studied elements using minimal tillage and no-till was almost 1.5–2 times higher than during moldboard ploughing. The use of resource-saving technologies provided a number of advantages over moldboard ploughing. Therefore, these improve various aspects of the relationship between crop and soil, such as the accumulation of SOM, improving water retention and infiltration, maintaining soil temperature, and soil microbiological and enzymatic activity (Franzluebbers, 2004; Malhi et al., 2018). The exchangeable fraction of Cu and Zn, which are essential nutrients for plants, increased during the use of resource-saving tillage systems compared to never-tilled soil (by 50% for Cu, 43% for Zn during minimal tillage and by 48% during the use of no-till in Ap horizon) (Table 3). The use of resource-saving technologies, including no-till together with an adequate dose of fertilizer for the good development of cultures and intensive care of crops, increase the content of exchangeable fraction of Zn and Cu compounds in the soil regardless of the nutritional status.

Migration processes of the trace elements

The leaching of the part of the total concentration of Pb and Cu to the underlying layers was observed in the never-tilled soil profile (Table 4). Similar distribution of Pb was also observed in the no-till soil profile. At the same time, Zn and Cu accumulated insignificantly in the surface layer (Table 4). Lead, Cu and Zn accumulation in organic horizons occurred during moldboard ploughing and minimal tillage.

Preservation of mulch on the surface due to the no-till implementation created favorable humidity and temperature conditions, promoted Zn and Pb exchangeable fraction accumulation in organic horizons. Whereas Cu was leached to the underlying horizons in the soil profile (Table 4).

A minimum accumulation coefficient characterizes the soil with use of moldboard ploughing. Prolonged use of moldboard ploughing leads to loss of SOM, over the consolidation of the arable and subsoil layers, and mechanical destruction of aggregates, which enhances erosion processes. As a result, a decrease in exchangeable fraction of the studied elements could be justified in these conditions. The leaching of all exchangeable fraction of the studied elements to the underlying layers of Haplic Chernozem was also observed using the minimal tillage method (Table 4).

Similar migration processes of the elements were also found in the never-tilled soil and no-till, and moldboard ploughing with minimal tillage (Table 4).

Trace elements interaction with soil organic matter (SOM)

The positive average dependence of the total Zn content ($r = 0.51$; at 0.95 confidence degree) on SOM was observed (Fig. 5a). The correlation was established between the exchangeable fraction of Cu and SOM ($r = -0.46$; at 0.95 confidence degree) (Fig. 5b). Soil organic matter is one of the important factors that may affect mobility and availability of Pb, Zn, Cu content in Haplic Chernozem. By analyzing both, total and exchangeable fraction of Pb, no significant dependence on SOM was observed (Fig. 5c). Perhaps, this occurred due to a high content of carbonates in the Bca horizon leading to a more active accumulation of Pb.

The higher content of SOM and close to the neutral reaction of the soil solution decreases the availability of Zn and Cu to plants (Gonzalez et al., 2015; Kabata-Pendias, 2010). The total content of Cu is accumulated in the upper soil layer with a higher content of SOM (Hooda, 2010; Wei et al., 2007). Our previous study

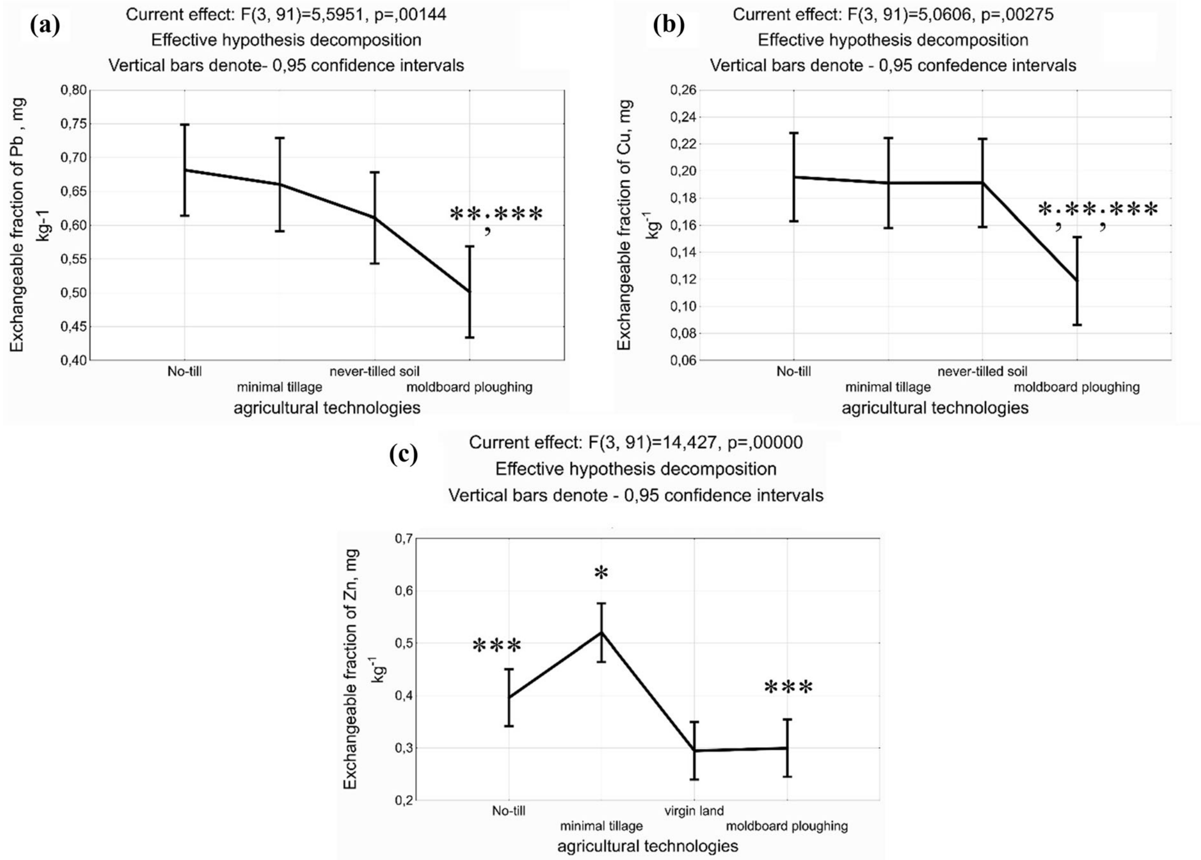

Fig. 4 Influence of agricultural technologies on the exchangeable fraction of **a** Pb, **b** Cu and **c** Zn in Haplic Chernozem (*significant statistical difference of element content between studied agrotechnologies and never-tilled soil; **significant statistical difference of element content between studied agrotechnologies and no-till; ***significant statistical difference of element content between studied agrotechnologies and minimal tillage)

Table 4 Coefficients of accumulation of total and exchangeable fraction of trace elements in the profile of Haplic Chernozem with various agricultural technologies

	Cultivation methods			
	No-till	Minimal tillage	Moldboard ploughing	Never-tilled soil
Total content of elements				
Pb total	0.89	1.10	1.33	0.93
Cu total	0.98	0.98	1.00	0.61
Zn total	1.08	1.07	1.12	1.07
Exchangeable fraction of elements				
Pb exchangeable fraction	1.09	0.68	0.63	1.19
Cu exchangeable fraction	0.41	0.36	0.24	0.30
Zn exchangeable fraction	1.77	0.87	0.75	1.54

showed that using of resource-saving technologies, including no-till, increases the SOM compared to moldboard ploughing (Medvedeva et al., 2021). The increase of SOM concentration during the use of no-

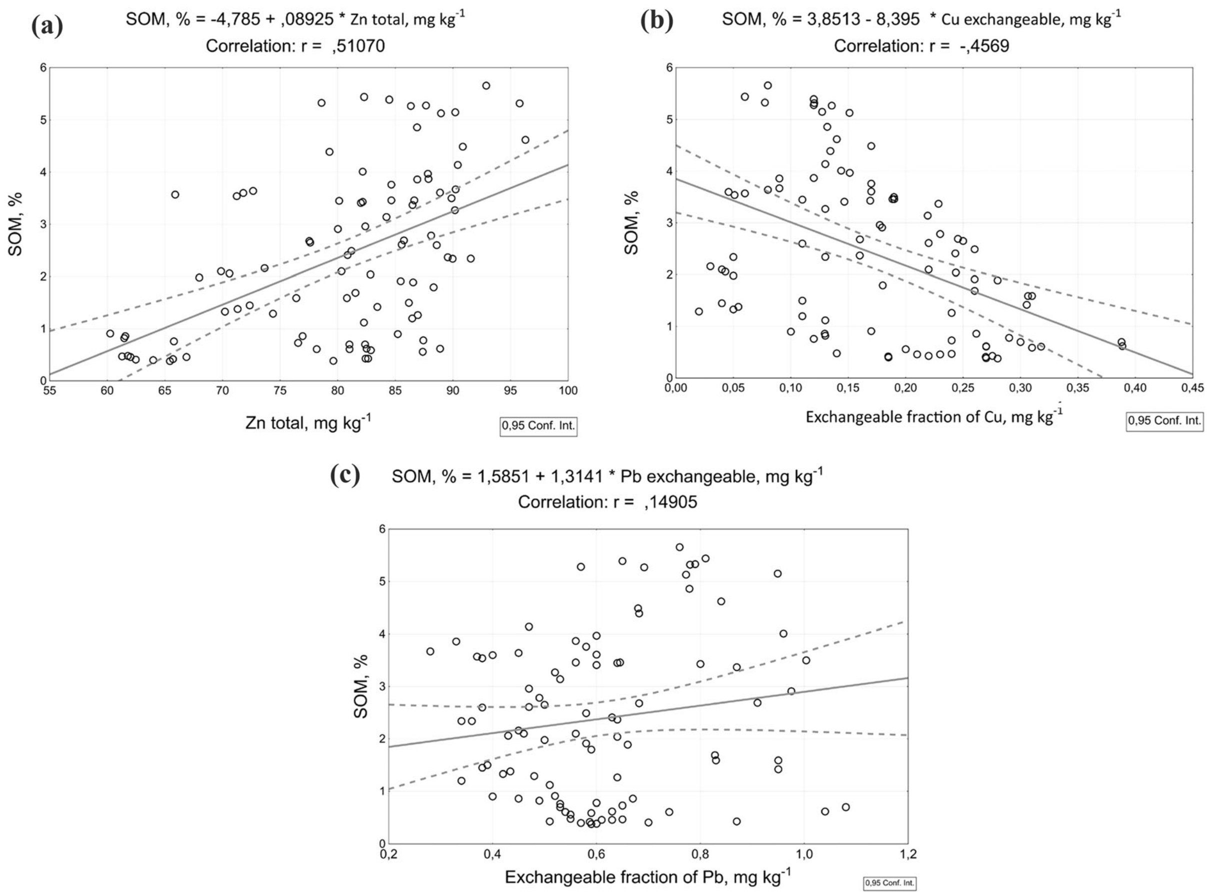

Fig. 5 The dependence of the elements' content on soil organic matter (SOM) within the profile of Haplic Chernozem, **a** Total content of Zn, **b** Exchangeable fraction of Cu and **c** Exchangeable fraction of Pb

till reduced the availability of Cu to plants (Moreira et al., 2019). Therefore, an increase of SOM in agricultural soil resulting in decreases of Cu availability requires the application of Cu-containing fertilizers.

Conclusions

The distribution of trace elements and their mobility in the Haplic Chernozem profile under using of different resource-saving technologies were studied for the first time. In all studied tillage technologies, the total content of trace elements could be represented by the following series: Zn > Cu > Pb. The introduction of resource-saving tillage technologies insignificantly affected the content of total Pb, while it led to increased Zn and Cu content. In this regard, the total content of Pb was observed to accumulate in the upper layer) and the lower level. Moreover, the total content of Cu was found to be evenly distributed within the soil profile, and the total content of Zn was higher in the upper soil layer.

The use of resource-saving agricultural technologies, including no-till, increases the content of exchangeable fraction of Zn, Cu, and Pb compared to moldboard ploughing. The content of Cu and Zn also increases almost by 50% by applying resource-saving tillage systems compared to the never-tilled soil. The content of the exchangeable fraction of the elements was found to be in decreasing order: Pb > Zn > Cu. The agricultural use of Haplic Chernozem resulted in a change in the types of distribution profiles of the studied elements' exchangeable fraction. The greatest differences were noted in the distribution pattern of Zn content, where the accumulative type of profile of the never-tilled soil after using all agricultural technologies changed to eluvial.

Despite the increase in the content of Pb, Cu, and Zu, the concentration of these elements did not exceed MPC and APC levels. As for the exchangeable fraction of Cu and Zu, their content was not enough for adequate plant nutrition. Maintaining soil fertility and improving the quality of crop production requires optimization of nutrition with macro- and microelements of crops, not only Zn and Cu.

Author contributions This study is a result of the full collaboration of all authors. AMM: Conceptualization, Supervision, Writing—manuscript preparation with contributions from all co-authors, Participated in all experiments and coordinated the data-analysis; OAB: Conceptualization, Supervision, Coordinated the data-analysis, Writing—review & editing; AVK: Carried out the experiments; YII: Carried out the experiment; TMM: Supervised the project; SSM: Writing—review & editing; MM: Review & editing.

Funding This work was supported by the project of the Ministry of Science and Higher Education of the Russian Federation [Grant Number 0852-2020-0029] and by Grant of the President of the Russian Federation for support of leading scientific schools [Grant Number NSh-2511.2020.11].

Data availability The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Declarations

Conflict of interest The authors declare that there is no conflict of financial interests or personal relationships regarding the publication of this paper.

Ethical approval Not applicable since the manuscript has not been involved the use of any animal or human data or tissue.

Consent to participate Not applicable.

Consent for publication Not applicable.

References

Acar, M., Celik, I., & Günal, H. (2018). Effects of long-term tillage systems on aggregate-associated organic carbon in the eastern Mediterranean region of Turkey. *Eurasian Journal of Soil Science, 7*(1), 51–58. https://doi.org/10.18393/ejss.335329

Artyushin, A. M., Florinsky, M. A., Lunev, M. I., Efremov, E. N., Sychev, V. G., & Kolokoltseva, I. V. (1992). *Methodological guide for determination of heavy metals in agricultural soils and plant products*. TsINAO. (in Russian).

Bauer, T. V., Minkina, T. M., Mandzhieva, S. S., Chaplygin, V. A., Nevidomskaya, D. G., Sushkova, S. N., & Bakoev, SYu. (2015). Background content and composition of zinc, copper and lead compounds in Haplic Chernozem of natural landscapes of the Rostov oblast. Nauchn. Zh. Ross. *Nauchno-Issled Inst Probl Melior, 4*(20), 186–199. in Russian.

Biryukova, O. A., Bozhkov, D. V., Minkina, T. M., Medvedeva, A. M., & Elnikov, I. I. (2015). Models of winter wheat yield based on calcareous chernozem fertility parameters. *American Journal of Agricultural and Biological Sciences, 10*(4), 186–196. https://doi.org/10.3844/ajabssp.2015.186.196

Burachevskaya, M., Minkina, T., Mandzhieva, S., Bauer, T., Chaplygin, V., Zamulina, I., Sushkova, S., Fedorenko, A., Ghazaryan, K., Movsesyan, H., & Makhinya, D. (2019). Study of copper, lead, and zinc speciation in the Haplic Chernozem surrounding coal-fired power plant. *Applied Geochemistry, 104*, 102–108. https://doi.org/10.1016/j.apgeochem.2019.03.016

Chang, H., Wang, Q., Li, Z., Wu, J., Xu, X., & Shi, Z. (2020). The effects of calcium combined with chitosan amendment on the bioavailability of exogenous Pb in calcareous soil. *Journal of Integrative Agriculture., 19*(5), 1375–1386. https://doi.org/10.1016/S2095-3119(19)62861-3

Dong, W., & Wang, Q. (2012). Experimental studies on the transport of copper down the soil profile and in runoff during rainfall. *Australian Journal of Crop Science, 6*(6), 1080–1087.

Figlioli, F., Sorrentino, M. C., Memoli, V., Arena, C., Maisto, G., Giordano, S., Capozzi, F., & Spagnuolo, V. (2019). Overall plant responses to Cd and Pb metal stress in maize: Growth pattern, ultrastructure, and photo-synthetic activity. *Environmental Science and Pollution Research, 26*(2), 1781–1790. https://doi.org/10.1007/s11356-018-3743-y

Fonseca, A. F., Caires, E. F., & Barth, G. (2010). Extraction methods and availability of micronutrients for wheat under a No-till system with a surface application of lime. *Scientia Agricola, 67*(1), 60–70. https://doi.org/10.1590/S0103-90162010000100009

Franzluebbers, A. J. (2004). Tillage and residue management effects on soil organic matter. In F. R. Magdoff & R. R. Weil (Eds.), *Soil organic matter in sustainable agriculture* (pp. 227–268). CRC Press.

Gavrilyuk F. Ya. (1955). *Chernozems of Western Ciscaucasia*. KhSU. **(in Russian)** .

Gonzalez, D., Almendros, P., & Alvarez, J. M. (2015). Mobility in soil and availability to triticale plants of copper fertilisers. *Soil Research, 53*(4), 412–422. https://doi.org/10.1071/SR14165

GOST 26107-84. (1984). *Soils. Methods for determination of total nitrogen*. Moscow. **(in Russian)**.

GOST 28168-89. (1989). *Nature protection. Soils. Sampling procedure.* Moscow. **(in Russian)**.

Herrera, J. M., Noulas, C., Stamp, P., Levy-Häner, L., Pellet, D., & Qin, R. (2020). Nitrogen rate increase not required for no-till wheat in cool and humid conditions. *Agronomy, 10*(3), 430. https://doi.org/10.3390/agronomy10030430

Hooda, P. A. (2010). *Trace elements in soils.* Blackwell Publishing Ltd.

Kabata-Pendias, A. (2010). *Trace elements in soils and plants* (4th ed.). CRC Press/Taylor & Francis Group.

Kachinski, W. D., Ávila, F. W., Lopes, M. M. M., Reis, A. R., Rampim, L., & Vidigal, B. J. C. (2020). Nutrition, yield and nutrient export in common bean under zinc fertilization in no-till system. *Ciência e Agrotecnologia, 44*(1), e029019. https://doi.org/10.1590/1413-7054202044029019

Konstantinova, E., Minkina, T., Nevidomskaya, D., Mandzhieva, S., Bauer, T., Zamulina, I., Burachevskaya, M., & Sushkova, S. (2021). Exchangeable form of potentially toxic elements in floodplain soils along the river-marine systems of Southern Russia. *Eurasian Journal of Soil Science, 10*(2), 132–141. https://doi.org/10.18393/ejss.838700

Kumar, A., Choudhary, A. K., Pooniya, V., Suri, V. K., & Singh, U. (2016). Soil factors associated with micronutrient acquisition in crops-biofortification perspective. In *Biofortification of food crops* (pp. 159–176.). Springer. https://doi.org/10.1007/978-81-322-2716-8_13

Li, J., Peng, Q., Liang, D., Liang, S., Chen, J., Sun, H., Li, S., & Lei, P. (2016). Effects of aging on the fraction distribution and bioavailability of selenium in three different soils. *Chemosphere, 144*, 2351–2359. https://doi.org/10.1007/s11104-018-03920-y

Mahar, A., Wang, P., Ali, A., Lahori, A. H., Awasthi, M. K., Wang, Z., Guo, Z., Wang, Q., Feng, S., Li, R., & Zhang, Z. (2018). Immobilization of soil heavy metals using CaO, FA, sulfur, and Na_2S: A 1-year incubation study. *International Journal of Environmental Science and Technology, 15*, 607–620. https://doi.org/10.1007/s13762-017-1427-7

Malhi, S. S., Légère, A., Vanasse, A., & Parent, G. (2018). Effects of long-term tillage, terminating No-till and cropping system on organic C and N, and available nutrients in a Gleysolic soil in Québec, Canada. *The Journal of Agricultural Science, 156*, 472–480. https://doi.org/10.1017/S0021859618000643

Martınez, C. E., & Motto, H. L. (2000). Solubility of lead, zinc and copper added to mineral soils. *Environmental Pollution, 107*, 153–158. https://doi.org/10.1016/S0269-7491(99)00111-6

Medvedeva, A., Buryukova, O., Kucherenko, A., Ilchenko, Ya., Chaplygin, V., Rajput, V. D., & Kizilkaya, R. (2020). Content of heavy metals in Haplic Chernozem under conditions of agrogenesis. *E3S Web Conference. APEEM* (Vol. 169, p. 01024). https://doi.org/10.1051/e3sconf/202016901024.

Medvedeva, A. M., Biryukova, O. A., Ilchenko, Y. I., Minkina, T. M., Kucherenko, A. V., Bauer, T. V., Mandzhieva, S. S., & Mazarji, M. (2021). Nitrogen state of Haplic Chernozem of the European part of Southern Russia in the implementation of resource-saving technologies. *Journal of the Science of Food and Agriculture, 101*(6), 2312–2318. https://doi.org/10.1002/jsfa.10852

Minkina, T. M., Mandzhieva, S. S., Burachevskaya, M. V., Bauer, T. V., & Sushkova, S. N. (2018). Method of determining loosely bound compounds of heavy metals in the soil. *MethodsX, 5*, 217–226. https://doi.org/10.1016/j.mex.2018.02.007

Minkina, T. M., Motuzova, G. V., Nazarenko, O. G., Kryshchenko, V. S., & Mandzhieva, S. S. (2008). Combined approach for fractioning metal compounds in soils. *Eurasian Soil Science, 41*(11), 1171–1179. https://doi.org/10.1134/S1064229308110057

Montgomery, D. R. (2007). Soil erosion and agricultural sustainability. *Proceedings of the National Academy of Sciences of the United States of America, 104*, 13268–13272. https://doi.org/10.1073/pnas.0611508104

Moreira, A., Moraes, L. A. C., & Schroth, G. (2019). Copper fertilization in soybean–wheat intercropping under no–till management. *Soil Tillage Research, 193*, 133–141. https://doi.org/10.1016/j.still.2019.06.001

Muchuweti, M., Birkett, J. W., Chinyanga, E., Zvauya, R., Scrimshaw, M. D., & Lester, J. N. (2006). Heavy metal content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe: Implications for human health. *Agriculture, Ecosystems & Environment, 112*, 41–48. https://doi.org/10.1016/j.agee.2005.04.028

Nevidomskaya, D. G., Minkina, T. M., Soldatov, A. V., Shuvaeva, V. A., Zubavichus, Y. V., & Podkovyrina, Y. S. (2016). Comprehensive study of Pb (II) speciation in soil by X-ray absorption spectroscopy (XANES and EXAFS) and sequential fractionation. *Journal of Soils and Sediments, 16*(4), 1183–1192. https://doi.org/10.1007/s11368-015-1198-z

Paul, J., Choudhary, A. K., Suri, V. K., Sharma, A. K., Kumar, V., & Shobhna, V. (2014). Bioresource nutrient recycling and its relationship with biofertility indicators of soil health and nutrient dynamics in rice–wheat cropping system. *Communications in Soil Science and Plant Analysis, 45*(7), 912–924. https://doi.org/10.1080/00103624.2013.867051

PND F 16.1.42-04. (2004). *The methodology for measuring the mass fraction of metals and metal oxides in powder soil samples by X-ray fluorescence analysis, federal service for environmental control*. Moscow. **(in Russian)**.

Protasova, N. A., Gorbunova, N. S., & Belyaev, A. B. (2015). Biogeochemistry of trace elements in Haplic Chernozems of Voronezh oblast. *Vestn. Voronezh. Gos. Univ., Ser.: Khim Biol Farm, 4*, 100–106. (in Russian).

Raskin, I., & Ensley, B. D. (2000). *Phytoremediation of toxic metals: Using plants to clean up the environment*. Wiley.

Ren, Z., Sivry, Y., Tharaud, M., Cordier, L., Li, Y., Dai, J., & Benedetti, M. F. (2017). Speciation and reactivity of lead and zinc in heavily and poorly contaminated soils: Stable isotope dilution, chemical extraction and model views. *Environmental Pollution, 225*, 654–662. https://doi.org/10.1016/j.envpol.2017.03.051

Rusakov, N. V., Kryatov, I. A., Tonetopiy, N. I., Gumarov. Zh. zh., & Pithyahia, N. V. (2009). *Approximately permissible concentrations (APC) of chemicals in soil: hygienic standards*. Federal Hygienic and Epidemiological Center of Rospotrebnadzor, Moscow. **(in Russian)**.

Shaimukhametov, MSh. (1993). On the method of determination of adsorbed Ca and Mg in chernozemic soils. *Pochvovedenie, 12*, 105–111.

Silva, S., Pinto, G., & Santos, C. (2017). Low doses of Pb affected *Lactuca sativa* photosynthetic performance. *Photosynthetica, 55*, 50–57. https://doi.org/10.1007/s11099-016-0220-z

Smurov, S. I., Agafonov, G. S., Grogorov, O. V., & Shelukhina, N. V. (2014). Influence of main tillage methods on the content of trace elements. *Dostizh. Nauki Tekh. APK, 5*, 5–7. (in Russian).

USS Working Group WRB. (2015). World reference base for soil resources 2014, update 2015. *International soil classification system for naming soils and creating legends for soil maps.* World Soil Resources Reports No. 106. FAO, Rome.

Vadyunina, A. F., & Korchagina, Z. A. (1986). *Methods for the study of the physical properties of soil*. Agropromizdat. (in Russian).

Vodyanitskii, Y., Minkina, T., & Bauer, T. (2021). Methods to determine the affinity of heavy metals for the chemically extracted carrier phases in soils. *Environmental Geochemistry and Health*. https://doi.org/10.1007/s10653-021-00955-6

Vorob'eva, L. A. (2006). *Theory and practice of chemical analysis of soils*. GEOS. (in Russian).

Wei, X., Hao, M., & Shao, M. (2007). Copper fertilizer effects on copper distribution and vertical transport in soils. *Geoderma, 138*(3/4), 213–220. https://doi.org/10.1016/j.geoderma.2006.11.012

Wuana, R. A., & Okieimen, F. E. (2011). Heavy metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation. *ISRN Ecology, 2011*, Article ID 402647. https://doi.org/10.5402/2011/402647.

Yong, S. K., Shrivastava, M., Srivastava, P., Kunhikrishnan, A., & Bolan, N. (2015). Environmental applications of chitosan and its derivatives. *Reviews of Environmental Contamination and Toxicology, 233*, 41–43. https://doi.org/10.1007/978-3-319-10479-9_1