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Comparing two methods of sequential fractionation in the study of copper compounds in Haplic chernozem under model experimental conditions

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Abstract

Purpose It is very important to obtain the information on the soils capacity to immobilize HMs and distribute them among soil components. The aim of this work was to study the fractional composition of Cu compounds in Haplic chernozem under model contamination conditions using different fractionation methods.

Materials and methods The fractional composition of copper compounds in Haplic Chernozem artificially contaminated with copper acetate has been studied under model experimental conditions. General regularities and differences in the distribution of Cu forms in soils at the use of sequential fractionation by the Miller method modified by Berti and Jacobs (1996) and the Tessier method (Tessier et al. 1979) are revealed.

Results and discussion The differences are related to the metal affinity for specific carrier phases, as well as to the selectivity and extraction capacity of the reagents used in these methods. A significant increase in the most mobile exchangeable Cu fraction is observed in contaminated soils. Aluminosilicates and soil organic matter make the largest contribution to the adsorption and retention of Cu.

Conclusions The Tessier method is more suitable for the separation of the total technogenic component from contaminated soils. The Miller method is more informative at the determination of loosely bound HM compounds because of the use of weaker extractants.

Keywords Compound forms · Copper · Extractant selectivity · Fractionation methods · Soils · Responsible editor: Jaume Bech

1 Introduction

The behavior of pollutants in the terrestrial ecosystems is characterized by their fractional composition rather than their total content in the soil. However, despite the half-century-long study of heavy metals (HMs) in soils, regularities of their fractional composition are insufficiently understood. At present, numerous procedures of sequential fractionation are used for the determination of the fractional composition of metals in soils, which calls for the revelation of specific effects of different extractants on the main phases carrying HMs and the comparative analysis of soils with different contents of HMs.

Sequential fractionation can assess the relative mobility of HMs and forms of their bonds with soil components. The method provides detailed information on the nature, occurrence forms, biological and physicochemical activity, mobility, and transportation of HMs (Chaplygin et al. 2014; Minkina et al. 2015).

The use of procedures with different stages, reagents, and extraction conditions showed that the obtained results are difficult to compare. The Bureau of the Commission of European Communities attempted to standardize the extraction procedure and developed a BCR fractionation scheme (1990). However, the new system has some disadvantages: reagents are insufficiently selective, readsorption of metals on organic

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and mineral components occurs, and significant differences between the sum of metal fraction and the total metal content in the soil are revealed (Raksasataya 1996; Mossop and Davidson 2003; Vodyanitskii 2006; Vodyanitskii and Yakovlev 2011). Therefore, the search for new optimal methods of extracting metal compounds from the soil and increasing the selectivity of extractants remain of current interest. To optimize the extraction of metals from soils by sequential fractionation, researchers change the order of extractions (Motuzova and Aptikaev 2006), apply the extractants generally used in parallel fractionation like 1 mol l^{-1} NH_4Ac and 1 mol l^{-1} HCl (Plekhanova and Bambusheva 2010; Kalent'eva and Panin 2011; Motuzova et al. 2014; Minkina et al. 2014c), reduce and optimize the time of extraction (Plekhanova and Bambusheva 2010), and vary the soil:solution ratio (Ladonin and Karpukhin 2011). To increase the information content of the obtained results, a hybrid fractionation scheme was proposed (Minkina et al. 2013; Mandzhieva et al. 2014), which is based on the results of sequential and parallel extraction and calculation approaches.

The uncertainty of methods for determining the content of HM compounds, their mobility and availability to plants, as well as problems in the comparison of the methods used, require further studies in this field. The problem should be solved with account for the regional distribution features of elements in soils.

Information on the capacity of soils to immobilize HMs and distribute them among soil components can be acquired not only from the analysis of technogenically contaminated soils, but also from model laboratory experiments. The artificial application of different rates of metals allows tracing the response of the soil system under varying technogenic load, comparing the results of natural and artificial contamination, and predicting the strength of metal fixation by the soil at different contamination levels. The use of high rates of pollutants makes it possible to reveal mechanisms of their transformation in the soil, especially under controlled conditions, when the role of natural factors is leveled. Laboratory modeling of soil contamination helps to neutralize the influence of environmental conditions such as temperature and water regime. This allows us to monitor more accurately the behavior of HM in the soil. Comparison of the results obtained in the investigation of technogenic-polluted soil and artificially contaminated soil shows general patterns in the distribution of the HM in the soil (Mandzhieva et al. 2014).

Copper is a priority pollutant of soils in southern Russia (Bauer et al. 2017; Minkina et al. 2017). Although Cu is a micronutrient for living organisms, it can have a toxic effect when present in high concentrations (Šeda et al. 2017). This calls for studying the content and occurrence forms of Cu in soils.

The aim of this work was to study the fractional composition of Cu compounds in Haplic chernozems under model contamination conditions using different fractionation methods.

2 Materials and methods

Soil for model laboratory experiments included samples from the humus-accumulative A_1 horizon of Haplic hernozem (WRB 2006) collected in the "Persianovskaya Steppe" Specially Protected Natural Territory, Rostov oblast, Russia.

The soil (1 kg) was air-dried, triturated using a pestle with a rubber head, and sieved through a 1-mm sieve. Plastic pots with a closed drainage system was used. Dry salt of Cu acetate were added to the soil at a rates of 300 and 2000 mg kg^{-1}. The soil was thoroughly mixed, wetted, and incubated for 1 year at room temperature and normal light mode. It is known (Minkina et al. 2015), that Cu, entered in easily soluble compounds in Haplic chernozem, has been transformed with different compounds formation in soil during 1 year.

The soil was constantly wetted at 0.6 of the maximum water capacity for best transformation of added copper compounds. Experiments were performed in triplicates. Analogous procedures but without addition of metal were performed with the control sample. After the end of incubation, an average sample was taken from each pot for analysis. The soil was brought to the dry state. The soil had the following properties (g kg^{-1}): Corg 0.37; $CaCO_3$ 0.04; physical clay 6.36; clay 2.81; pH_{H2O} 7.6; exchangeable bases ($cmol_c$ kg^{-1}): Ca^{2+} 31.0, Mg^{2+} 6.0, Na^+ 0.06. Data on exchangeable bases were obtained according to the Shaymukhametov method (Shaimukhametov 1993). The principle of the method is based on the ability of the ammonium cation of a solution of acetic acid and 1 N ammonium chloride to displace the exchangeable cations, the pH of the solution 6.5.

The composition of Cu compounds was analyzed using two sequential fractionation methods: the Tessier method (Tessier et al. 1979) ensuring the separation of five HM fractions and the Miller method (Miller et al. 1986) modified by (Berti and Jacobs 1996), which separates eight HM fractions in the soil (Table 1). The Tessier method (Tessier et al. 1979) is one of the most common procedures used for the sequential fractionation of HMs. This method was developed for studying potentially hazardous elements in bottom sediments. However, it soon found use for soils (Bacon and Davidson 2008). Along with the Tessier method, the Miller method (Miller et al. 1986) modified by Berti and Jacobs (1996), which extracts larger amounts of HMs from soils, is of interest. By the Miller method, the water-soluble and exchangeable fractions are isolated separately, while only the exchangeable fraction is isolated by the Tessier method (Table 1). To compare the results of two fractionation methods, the first two fractions by the Miller method (water-soluble and exchangeable ones) were combined and considered as the

Table 1 Extractants for the fractionation of heavy metal compounds

Extraction conditions	Fractions							
	Water-soluble[a]	Exchangeable[a, b]	Bound to carbonates[a, b]	Bound to Mn oxides[a]	Bound to Fe and Mn[b]	Bound to organic matter[a, b]	Bound to amorphous Fe oxides[a]	Bound to crystalline Fe oxides[a]	Residual[a, b]
The Miller method modified by Berti and Jacobs (1996)									
The extractant	Bidistilled water	0.5 M $Ca(NO_3)_2$ pH 7 (using CaO)	0.44 M CH_3COOH + 0.1 M $Ca(NO_3)_2$	0.1 M $NH_2OH{\cdot}HCl$ + 0.01 M HNO_3	–	0.1 M $Na_4P_2O_7$	0.175 M $(NH_4)_2C_2O_4$ + 0.1 M $H_2C_2O_4$ (Tamm reagent)	0.175 M $(NH_4)_2C_2O_4$ + 0.1 M $H_2C_2O_4$ (ultraviolet)	HF + $HClO_4$ after HNO_{3conc} evaporation
The ratio of soil:solution	1:10	1:10	1:10	1:14	–	1:14	1:14	1:14	1:14
The Tessier method (Tessier et al. 1979)									
The extractant	–	1 M $MgCl_2$	1 M CH_3COONa + CH_3COOH	–	0.04 M $NH_2OH{\cdot}HCl$ with 25% CH_3COONH_4	30% H_2O_2 + HNO_3 pH 2 after 3.2 M CH_3COONH_4	—	—	HF + $HClO_4$ after HNO_{3conc} evaporation
The ratio of soil:solution	–	1:8	1:8	–	1:20	1:20	–	–	1:25

[a] Fraction, determined by the Miller method modified by Berti and Jacobs (1996)

[b] Fraction, determined by the Tessier method (Tessier et al. 1979)

exchangeable fraction. To compare the results of two fractionation procedures, the contents of metals in the fractions bound to amorphous Fe oxide and crystalline Fe and Mn oxides obtained using the Miller scheme were summarized (Table 1).

Analysis of HM content in soil extracts was determined by atomic absorption spectrophotometry. The total HM content in the soils of model experiment was determined by X-ray fluorescence on spectroscan "MAKC-GV."

The results of chemical analysis correspond to the mean of three replicates. Descriptive data analysis, comprising minimum value, mean value, maximum value, and standard deviation, was carried out with Excel 2010.

3 Results

The content of Cu in the studied uncontaminated soil is lower than the maximum permissible concentration (MPC = 55 mg kg^{-1}) (Artyushin 1992) and insignificantly exceeds the background level (29.0–40.0 mg kg^{-1}) (Akimtsev et al. 1962; Kovalskii and Andrianova 1970; Khoroshkin and Khoroshkin 1979) and the clark for soils (20 mg kg^{-1}) (Vinogradov 1957) (Table 2).

The following Cu distribution of fraction forms in the native uncontaminated Haplic chernozem was determined by the Miller method (Table 2, Fig. 1): residual Cu > Cu bound to organic matter > Cu bound to crystalline Fe oxides > Cu bound to carbonates > Cu bound to Mn oxides > exchangeable Cu > water-soluble Cu.

The content of most mobile Cu fractions (Fig. 1) in the uncontaminated soil is no more than 3% (water-soluble, exchangeable, bound to carbonates, and Mn oxides-bound fractions). The content of the bound to carbonates fraction is 3–5 times higher than the content of the exchangeable fraction (Table 2). The fractions bound to Fe and organic matter contain 8 to 12% Cu (Fig. 1). In uncontaminated soils, the major part of Cu (up to 67% of the total content) is retained in the crystalline lattices of primary and secondary minerals (Fig. 1), which makes them inaccessible for living organisms.

At the addition of metal to the soil at rates of 300 and 2000 mg kg^{-1}, the total Cu content increases and exceeds the MPC in 6 and 37 times, respectively (Table 2).

Changes in the fractional composition of the metal are observed under contamination. Cu percentage increases highly in the most mobile fractions (Fig. 1): in 2.5 times in the water-soluble (from 0.2 to 0.5%) and exchangeable (from 0.2 to 1%) fractions and in 4.3–15.7 times in the bound to carbonates fraction (from 0.7 to 3 and 11%). The percentage of Cu bound to organic matter increases in 2.3–2.4 times (from 12 to 27 and 29%), which almost equivalents Cu percentage in the residual fraction in soil with 300 mg/kg of Cu (Fig. 1).

Table 2 Fractional composition of Cu in Haplic chernozem of model experiment determined by the Miller method modified by Berti and Jacobs (1996), mg kg^{-1} ($n = 9$)

Added dose, mg kg^{-1}	Fractions									Total content
	Water soluble	Exchangeable	Bound to carbonates	Bound to Mn	Bound to organic matter	Bound to amorphous Fe oxides	Bound to crystalline Fe oxides	Residual	Sum	
Uncontaminated soil (control)	0.1 ± 0.1	0.1 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	5.1 ± 1.1	3.2 ± 0.2	4.2 ± 0.4	27.5 ± 4.5	41.0 ± 3.1	44.0 ± 3.6
300	0.2 ± 0.1	2.7 ± 0.5	36.9 ± 4.1	13.8 ± 2.1	91.9 ± 8.8	61.6 ± 5.6	42.9 ± 6.1	87.0 ± 7.9	337.0 ± 23.7	343.0 ± 21.1
2000	9.4 ± 1.5	27.2 ± 3.4	69.1 ± 5.5	68.2 ± 4.9	592.7 ± 20.1	246.2 ± 19.8	106.5 ± 10.2	899.7 ± 39.2	2019.0 ± 48.0	2049.0 ± 44.1

The Cu percentage increases in 1.5–2.3 times in the fractions bound to amorphous Fe oxides (from 8 to 12 and 18%) and in 3–4 times in the fractions bound to Mn oxides (from 1 to 3 and 4%), while its share in the fractions of crystalline Fe forms decreases (Table 2).

The concentration of Cu compounds bound to amorphous Fe increases, which affects the metal distribution among the fractions under contamination (Fig. 1): residual Cu > Cu bound to organic matter > Cu bound to amorphous Fe oxides > Cu bound to crystalline Fe oxides > Cu bound to carbonates > Cu bound to Mn oxides > exchangeable Cu > water-soluble Cu.

4 Discussion

4.1 Comparison of results obtained by different sequential fractionation methods

The Cu distribution among the fractions in the studied soils also was determined by the Tessier method, to reveal similarities and differences in the obtained data. The Cu distribution was following in the uncontaminated soil (Table 3, Fig. 2): residual Cu > Cu bound to organic matter > Cu bound to Fe-Mn oxides > Cu bound to carbonates > exchangeable Cu.

The role of organic matter and oxides of Fe-Mn increased the binding Cu under contamination. Content of these fractions dominates over the residual fraction, bound to carbonates and exchangeble Cu. Also the Cu percentage of exchangeable fractions increased in two times (from 1 to 2%), and the fraction associated with carbonates increased more than two times (from 3 to 8%) (Fig. 2).

Exchangeable fraction The contents of the exchangeable Cu fraction determined in the native and contaminated soils by the Tessier method are up to two times higher than those determined by the Miller method (0.5 and 1%) (Fig. 2), which is related to the higher concentration and dispersing capacity of the $MgCl_2$ extractant. The preferred use of $Ca(NO_3)_2$ solution for the extraction of exchangeable HM ions by the Miller method should also be noted in relation to the requirements for the cation of the displacing salt (Gorbatov and Zyrin 1987), which does not overestimate the result, in contrast to $MgCl_2$.

Fraction bound to carbonates The contents of Cu in carbonate-bound fraction from the native soil determined by two methods differ, despite of similar reagents, which used in both methods (Berti and Jacobs 1996; Tessier et al. 1979). In contaminated samples, the content of Cu in the carbonate fraction increases abruptly, especially when the Miller method is used (Table 3, Fig. 2). The significant increase of the Cu content in the bound to carbonates fraction is related to the presence of dispersed carbonate forms in Haplic chernozem.

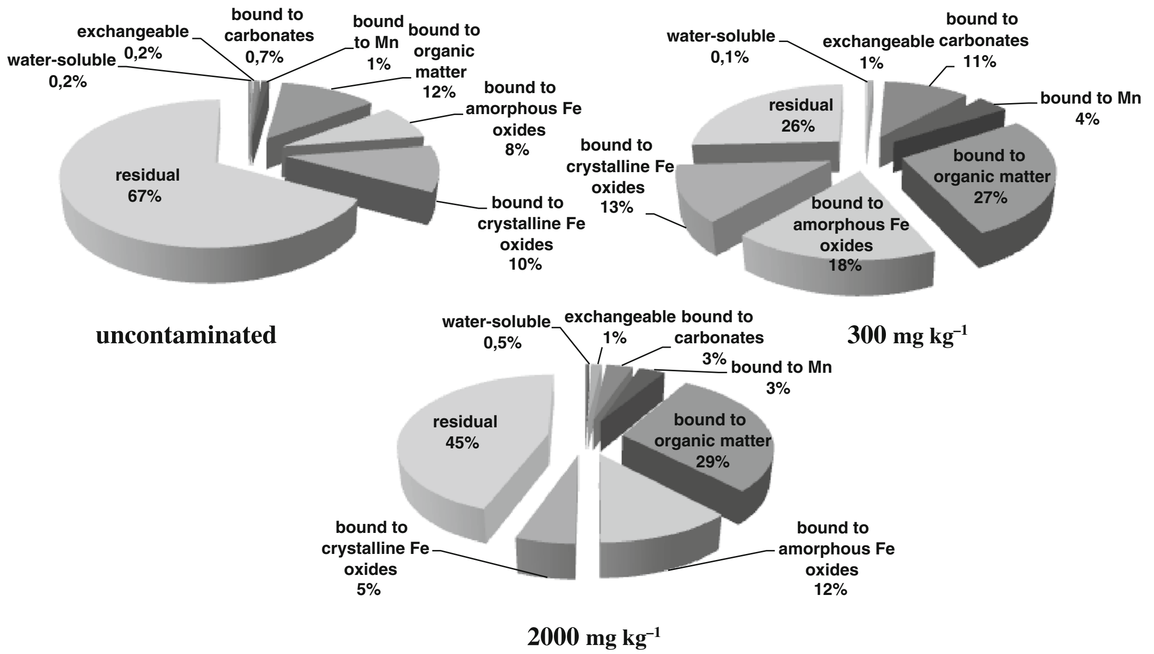

Fig. 1 Fractional distribution of Cu determined by the Miller method modified by Berti and Jacobs (1996), % of the sum of fractions

Dispersed carbonates have a high specific surface area, which increases their interaction with HMs.

Fraction bound to Fe–Mn oxides Analysis of the X-ray absorption near edge structure (XANES) spectra (Minkina et al. 2016) showed that the Cu^{2+} ions adsorbed by the soil can substitute some Al^{3+} ions in the octahedral positions of clay minerals. Adsorption of copper in the form of dimer (Cu–Cu) by silicate and/or aluminum groups with incomplete coordination or structural defects (changes in bond lengths, appearance of double bonds) is also possible.

In Haplic chernozem, the percentage of Cu in Fe–Mn oxides is 19 to 35% (Fig. 2). The content of Cu in Haplic chernozem determined by the Tessier method is higher than that determined by the Miller method by 3% (Fig. 2). This can be related to the use of a strong reducer, high treatment temperature (96 °C), and a high concentration of 4175 mol L^{-1} CH_3COOH, which can affect other soil components (Vodyanitskii and Yakovlev 2011).

The separation of the Mn oxide-bound fraction by the Miller method is especially important for soils with high Mn contents. In the studied soil, the content of Mn oxide is low: 860 mg kg^{-1} (Mn clark for soils is 850 mg kg^{-1} (Vinogradov 1957)). The technogenic metal compounds are transformed mainly in compounds bound to amorphous Fe oxides. The capacity of adsorbing freshly precipitated hydroxides is higher than for crystalline ones; the adsorption of HMs hampers the crystallization of amorphous hydroxides (Yakovlev et al. 2008; McBride 1981). The crystallization of Fe oxides is a relatively long process, and an abrupt increase in the content of HMs in amorphous Fe indicates a recent contamination. Thus, more significant increase in the content of Cu bound to amorphous Fe oxides compared to Cu bound to crystalline Fe oxides can indicate the technogenic input of the metal into the soil.

In the soil with a Cu application rate of 300 mg kg^{-1}, the content of Cu bound to Fe and Mn oxides increases in almost two times at the use of the Miller method (35%) and in 1.5

Table 3 Fractional composition of Cu in Haplic chernozem of model experiment determined by the Tessier method (Tessier et al. 1979), mg kg^{-1} ($n = 9$)

Added dose, mg kg^{-1}	Fractions					
	Exchangeable	Bound to carbonates	Bound to Fe and Mn	Bound to organic matter	Residual	Sum
Uncontaminated soil (control)	0.4 ± 0.1	1.2 ± 0.3	10.0 ± 2.2	16.1 ± 4.3	17.3 ± 2.4	45.0 ± 5.4
300	6.5 ± 1.1	27.8 ± 3.2	116.4 ± 10.4	110.1 ± 9.9	80.2 ± 8.6	341.0 ± 22.7
2000	47.4 ± 4.1	62.7 ± 4.9	493.1 ± 27.9	772.3 ± 39.3	657.5 ± 45.6	2033.0 ± 55.0

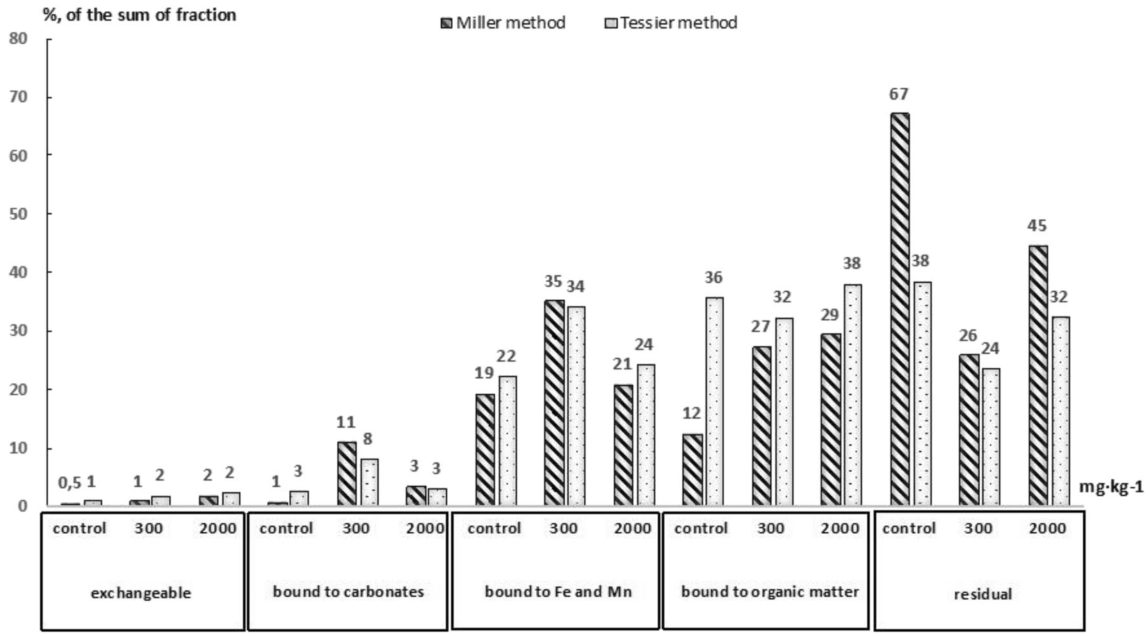

Fig. 2 Fractional distribution of Cu determined by the Miller method (Miller et al. 1986) modified by Berti and Jacobs (1996) and the Tessier method (Tessier et al. 1979), % of the sum of fractions

times at the use of the Tessier method (34%) compared to the uncontaminated soil, while the difference is lower at the higher contamination rate (2000 mg kg^{-1} Cu) (Fig. 2).

Fraction bound to organic matter The role of organic matter in the binding of Cu increases with the high doses of the pollutant applying. So, when using the method of Miller, metal content in this fraction increased more than two times (from 12 to 29%) (Fig. 2). Active interaction of copper with organic matter is best manifested during fractionation by the Tessier method. In soils with a contamination rate of 300 mg kg^{-1}, the content of Cu in organic matter exceeds that in the fraction bound to aluminosilicates (Fig. 2). Obviously, the more aggressive reagents, which are used in a method Tessier, destruct the clay minerals structure.To extract Cu bound to soil organic matter by the Miller method, humic acids are dissolved under alkalinemedia, and HM ions are retained in the solution due to the strong complexing capacity of pyrophosphate ions. The application of an alkaline extractant has significant limitations.

Extractant also affects mineral soil components, which can result in the overestimation of results. It was shown (Vodyanitskii 2013; McLaren and Crawford 1973) that 0.1 mol L^{-1} $Na_4P_2O_7$ can partially dissolve clay minerals and crystalline Fe. The selectivity of analysis can be improved by the preliminary separation of exchangeable and carbonate-bound compounds and Mn-oxide bound HM ions from the test soil sample.

Another group of methods for removing metals retained by organic matter is based on its completed decomposition. It includes the Tessier method, when an acidic solution of hydrogen peroxide is used, which can completely decompose organic matter during the interaction with the soil. However, clay minerals and nonsilicate iron compounds can be affected simultaneously (Ladonin and Karpukhin 2011).

The capacity of soils to bind Cu strongly depends on the nature and amount of organic matter in soils. It is known that humic and fulvic acids can form stable complexes with Cu and that organic matter can affect some reactions of Cu with inorganic soil components (Kabata-Pendias and Pendias 1989; Adriano 2001; Plekhanova et al. 2001; Mandzhieva et al. 2014; Minkina et al. 2014b).

Residual fraction When the Miller method is used, the predominant part of metal, upto 67% on the average, is retained in the crystalline lattices of primary and secondary minerals of uncontaminated soils (Fig. 2).

The content of Cu in the residual fraction determined by the Miller method is higher than that determined by the Tessier method (Tables 2 and 3, Fig. 2). This indicates the use of more aggressive extractants capable of extracting, along with previous fractions, some HMs bound to soil minerals by the Tessier method, that may also be associated with a lower ratio of soil:solution (Table. 1).

The decrease in the content of Cu in the residual fraction in 1.2–2.6 times under contamination, which is revealed by both Tessier and Miller methods, indicates a preferential interaction of Cu with native soil components: organic matter, carbonates, Fe–Mn oxides (Minkina et al. 2014a).

5 Conclusions

1. Regularities in the changes of Cu fractional composition in Haplic chernozem under contamination determined by sequential fractionation using the Miller method modified by Berti and Jacobs (1996) and the Tessier method (Tessier et al. 1979) are largely analogous.
2. Differences in the results of HM fractionation from the soil are due to the higher extraction capacity of the reagents used by the Tessier method than those by the Miller method during the separation of Cu bound to organic matter and Fe and Mn oxides. The differences are higher for the contaminated soil. The Tessier method is more suitable for the separation of the total technogenic component from contaminated soils. The Miller method is more informative at the determination of loosely bound HM compounds because of the use of weaker extractants.
3. Organic matter, nonsilicate iron, and carbonates compounds are the main components that retain Cu coming into the soil at high pollution. The contamination of soil results in an increase in the content of Cu bound to amorphous Fe forms. In Cu-contaminated soil, the relative content of metal in the residual fraction decreases, and the percentage of the most mobile metal fractions increases, regardless of the extraction method.

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