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Methodological aspects in the analysis of the content of mobile compounds of heavy metals in hydromorphic soils



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ABSTRACT

The content of mobile compounds of Zn, Pb and Cu in the hydromorphic soil samples with natural humidity from southern European Russia turned out to be much higher than in samples stored in laboratory for 1 month and, particularly, 3 years. At the same time, the extractability of heavy metals is characterized by irregular kinetics: their solubility decreases rapidly during the first month when the dry soil sample loses the initial humidity, but slowly during its further storage for 3 years. Solubility of metals in natural humid soils is highly variable. Influence of the studied reagents (CH₃COONH₄, EDTA and oxalate) shows the following general trend: Zn > Pb \gg Cu. Solubility difference of metals is smoothed over in the course of soil drying. In terms of the dissolution efficiency of mobile metal compounds in the hydromorphic ferruginated soils, the extractants are arranged in the following order: oxalate > EDTA > CH₃COONH₄. Since the oxalate actively dissolves Fe(II)-compounds in soils, the solubility of metal is governed by the its siderophility. Zn is most intensely dissolved by oxalate, while Pb and Cu in soils demonstrate organophilic properties. However, Pb can also be sorbed on iron hydroxide particles.

1. Introduction

It is necessary to define the mobile forms of heavy metals (HM) in soils to substantiate measures aimed at remediating polluted areas. Mobile forms of HM govern the choice of a certain method for the reclamation of a contaminated area when designing artificial geochemical permeable barriers or other methods of soil remediation: chemical method, introduction of sorbents and biological reclamation by incubating specific cultures (super-accumulators) of HM (Elliott, Herzig, 1999; Elliott, Shastri, 1999).

There are numerous methods for fractionating HM compounds in soil depending on their bond strength with the pedogenic components (Elliott, Herzig, 1999; Elliott, Shastri, 1999; Ma, Uren, 1995; Sun et al., 2001; Vodyanitskii, 2006; Minkina et al., 2008; Mandzhieva et al., 2016). The content of mobile HM forms is determined based on their solubility in different reagents. Solubility of HM compounds in "weak" reagents reflects the different stability of compounds defined by the common notion of "mobile". It is important to know the exact content of mobile HM compounds in soils.

At present, soil samples are usually transported without the preservation of their natural humidity and the subsequent storage at room

temperature in an oxidative environment, resulting in soil drying. Laboratory extraction of HM is based on methods adapted for dry soils.

However, many properties of the initial soil change significantly after the drying, particularly, if the soil is hydromorphic (Bartlett, James, 1980; Kersten, Forstner, 1986; Haynes, Swift, 1991; Tome et al., 1996; Vodyanitskii, Makarov, 2016; Kalambukattu et al., 2018). Variations in the redox potential of medium provoke the most intense changes in properties of both mineral and organic phases of soil. In the mineral phase, the strongest response to the elimination of reductive conditions is demonstrated by elements with a variable valency, such as Fe, Mn, As, Cr and U (Phillips et al., 1993; Ross et al., 2001). Mobility of siderophiles like Zn in soils enriched with iron oxides (Kirpichtchikova et al., 2006) also can change in the course of sample drying.

Two antipathetic scenarios are possible: (i) direct effect if the soil drying decreases the content of mobile heavy metals; (ii) reverse effect if the drying increases their content. Particularly important is analysis of the influence of drying on the HM content in the polluted hydromorphic soils with high natural humidity.

Determination of the content of mobile HM compounds is commonly based on three types of reagents: (1) acetate processing with the acetate– ammonia buffer with pH 4.80 (1N CH₃COOH) or 0.43M CH₃COOH; (2)

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oxalate processing with the acid ammonium oxalate $0.14M H_2C_2O_4 + 0.20 M (NH_4)_2C_2O_4$ by the Tamm method or with $0.1M (NH_4)_2C_2O_4$ (pH = 3.2); and (3) complexonate processing with EDTA or its homologues.

Although such discrimination of mobile HM compounds into three groups is rather conditional because it provides a general insight into priority fractions of the mobile HM in both dry and wet samples. The content of these three fractions of the mobile HM compounds is determined during the parallel extraction (Minkina et al., 2018b). There is a need to examine a new sample preparation procedure using three reagents as examples, which can extract different groups of mobile HM compounds.

Copper, lead and zinc often occur together in metal contaminated ecosystems since they are frequently accompanied in industrial, urban, and agricultural applications, posing risks to human and ecosystem health. These elements have different affinities with sorption sites of organic and mineral phases in soil, thereby distributing into different chemical forms and exhibiting varying availability, mobility, and toxicity (Minkina et al., 2018c; Ren et al., 2017). The strong response of these elements to the conditions for preparing the soil sample for analysis is determined by their siderophilicity, due to the connection of Fe as an element with a change in valency.

The paper is aimed at: (1) to develop a sample preparation technique of the hydromorphic soils with the consideration of natural humidity for determining of contents of the HM mobile compounds; (2) based on the new sample preparation technique to compare the efficiency of three reagents (CH₃COONH₄, EDTA and oxalate) in dissolving different groups of mobile Cu, Pb and Zn compounds before and after the storage of dry samples.

2. Objects and methods

2.1. Studied objects

Hydromorphic soils of two types taken 450–500 m south and southeast of the Fillipenkov Settlement on the Glubokaya River terrace (Kamensk area, Rostov region, Russia) were studied. Type 1, classified as hydromorphic technisol (Technisols), is intensely waterlogged and polluted mainly with inorganic materials (Cu, Pb and, particularly, Zn) transported from Lake Atamanskoe that was exploited as sludge collector in the 1950's. Samples D3 and D4 were taken from the upper soil layer (0–20 cm). The analytical results are as follows: carbonates 0.4–1.1%, C_{org} 1.4–1.7%, silty particles (<1 µm) 25–33%, pH_{aq} 7.7–8.0.

Type 2 represents the hydromorphic carbonate vertisol (Vertisols) developed on alluvial clays away from the paleolake Atamanskoe. Sample P9 taken from the upper soil layer (0–20 cm) were analysed. The analytical results are as follows: carbonates 1.5%, C_{org} 2.4%, silty particles (<1 μ m) 20%, pH_{aq} 8.0.

2.2. Methods

New method for determining the content of metals in the initial wet samples was proposed.

The wet soil sample taken from the section was placed in a hermetically sealed polyethylene packet, transported to the laboratory in a refrigerator and stored under anaerobic dark conditions at +4 to +6 °C. The soil samples were analysed using the technique of parallel HM fractionation at natural humidity and after two periods of drying: shortterm (1 month) and long-term (3 years). This temporary series reflects contrasting differences in storage conditions of samples (fresh samples, samples with partial moisture loss and heavily dried samples). Dry soil samples were sifted through a 1 mm sieve to remove large particles and plant residues before being ground with a pestle and mortar (Minkina et al., 2018b).

Preliminarily, the humidity of the sample was determined to correct the wet sample mass. Soil moisture was determined by drying at 105^{0} in an oven to constant weight. This procedure made it possible to

determine the influence of humidity and duration of dry sample storage on the content of different groups of the mobile HM compounds.

The bulk content of Cu, Zn and Pb in soils was determined by the XRF method with a SPECTROSCAN MAKC-GV spectrometer. The content of the mobile compounds of metals was determined with: 1N CH₃COONH₄ with pH = 4.8, 1% EDTA solution in 1 N CH₃COONH₄ with pH = 4.8 and acid ammonium oxalate 0.14M H₂C₂O₄ + 0.20 M (NH₄)₂C₂O₄ by the Tamm method. The 1% CH₃COONH₄ with pH = 4.8 presumably capable of solubilizing exchangeable forms of metals. The 1% EDTA simulates organic acids emitted by plant risosphere and presumably capable relatively unstable complexes of metals. Tamm reagent presumably capable HM bound to amorphous Fe oxide and non-crystalline Fe (Minkina et al., 2018a; Vodyanitskii, 2001).

The content of the mobile compounds Cu, Zn and Pb was expressed in mmol/kg. The relative efficiency of reagent (*p*) in terms of HM dissolution was estimated in %:

$p = 100(\text{HM}_{\text{mob}}/\text{HM}_{\text{bulk}}),$

where $\rm HM_{mob}$ and $\rm HM_{bulk}$ are, respectively, the mobile and bulk content of HM.

3. Results

In studied soil humidity in fresh samples is much higher than in the dried samples (Table 1). Particularly water-saturated are Technisols: their natural humidity is as much as 38–41%. Vertisols are less water-saturated (only up to 21%).

The storage of soils for 1 month provoked an intense decrease of humidity down to 4.4–4.7%. Further storage for 3 years decreased humidity insignificantly (4.0–4.3%). Therefore, decrease in the HM solubility during the first month of storage is likely related to the loss of moisture, whereas the further decrease is caused by crystallisation of the readily soluble HM compounds.

3.1. Content of the sorbed CH₃COONH₄-soluble HM compounds

Zinc. In hydromorphic Technisols at natural humidity, the 1N CH_3COONH_4 solution can dissolve 29–47% of the bulk Zn content, whereas extractability of metal decreases to 16–26% after the soil drying for 1 month and to 17–20% after storage for 3 years. Note that the soil samples are strongly polluted, with the Zn content reaching 949–1010 mmol/kg.

In hydromorphic Vertisols, the humus horizon is also polluted with Zn: its bulk content (9.5 mmol/kg) is 9 times higher than the European Clarke value (1.04 mmol/kg) (Kabata-Pendias, 2011). From Vertisols at natural humidity, 1N CH₃COONH₄can extract as much as 52% of the bulk Zn content, whereas the extractability decreases to 37% after laboratory storage for 1 month and 35% after 3 years (Table 2).

Lead. In hydromorphic Technisols at natural humidity, 1N CH_3COONH_4 dissolves 9–28% of the bulk Pb content and a similar amount of metal after storage for approximately 1 month. Extractability decreases to 5–17% after sample storage for 3 years.

In hydromorphic Vertisols, the Pb content is at the European Clarke level (0.15 mmol/kg). At natural humidity, the $1N CH_3COONH_4$ solution extracts 18% of the bulk Pb content. The extractability of Pb decreases to 9 and 11%, respectively, after the sample storage for 1 month and 3 years (Table 2).

Table 1Humidity of soil samples (%).

Sample	Fresh	Storage duration 1 month	Storage duration 3 years
D3	44.1	4.4	4.1
D4	38.0	4.6	4.0
Р9	20.8	4.7	4.4

Table 2

Content of the extractable HM in Technisols and Vertisols at natural humidity and after laboratory storage for 1 month and 3 years.

Sample	Sample Total Dimension		Fresh 2019			Storage duration 1 month			Storage duration 36 months		
	content		1N CH ₃ COONH ₄	EDTA in 1N CH ₃ COONH ₄	Oxalate	1N CH ₃ COONH ₄	EDTA in 1N CH ₃ COONH ₄	Oxalate	1N CH ₃ COONH ₄	EDTA in 1N CH ₃ COONH ₄	Oxalate
Zn											
D3	1010	mmol/kg	477	539	546	159,5	365	406	167	387	378
		p (%)	47	53	54	16	36	40	17	38	37
D4	949	mmol/kg	275	365	435	247,3	348	402	189	361	395
		p (%)	29	38	46	26	37	42	20	38	42
P9	9,5	mmol/kg	5	5,7	6,9	3,5	4,3	5,9	3,3	4,5	5
		p (%)	52	60	72	37	45	61	35	47	53
Mean		p (%)	43	50	57	26	39	48	24	41	44
			50			38			36		
Pb											
D3	1.08	mmol/kg	0.096	0.312	0.424	0.088	0.299	0.36	0.058	0.263	0.347
		p (%)	9	29	39	8	28	33	5	24	32
D4	7.68	mmol/kg	2.137	3.387	3.73	2.069	2.749	3.036	1.284	2.229	2.652
		p (%)	28	44	49	27	36	40	17	29	35
P9	0.15	mmol/kg	0.027	0.072	0.082	0.014	0.046	0.041	0.016	0.037	0.051
		p (%)	18	48	55	9	31	27	11	25	34
Mean		p (%)	18	40	48	15	32	33	11	26	34
			35			27			24		
Cu											
D3	5.901	mmol/kg	0.045	0.13	0.299	0.041	0.119	0.213	0.031	0.067	0.183
		p (%)	0.8	2.2	5.1	0.7	2	3.6	0.5	1.1	3.1
D4	2.313	mmol/kg	0.054	0.142	0.215	0.042	0.099	0.169	0.043	0.057	0.135
		p (%)	2.3	6.1	9.3	1.8	4.3	7.3	1.9	2.5	5.9
P9	0.818	mmol/kg	0.014	0.078	0.097	0.007	0.057	0.075	0.01	0.048	0.069
		p (%)	1.8	9.6	11.9	0.9	7	9.2	1.2	5.9	8,5
Mean		p (%)	2	6	9	1	4	7	1	3	6
			5			4			3		

Copper. From hydromorphic Technosols at natural humidity, the 1N CH_3COONH_4 solution extracts less than 3% of the bulk Cu content, but less than 2% after the sample drying and storage for 1 month and 3 years.

In hydromorphic Vertisols, the humus horizon is polluted with Cu: its bulk content (0.82 mmol Cu/kg) is three times higher than the European Clarke level (Kabata-Pendias, 2011). The 1N CH_3COONH_4 solution can dissolve less than 2% of the bulk Cu content from this soil at natural humidity (Table 2). Moreover, the mobile forms of this metal tend to decrease with the duration of sample storage. This is due to transformational processes, lack of plants and weak microbiological activity of dry soils, in contrast to freshly selected soil samples. However, the main reason is the reduction processes cease during drying of hydromorphic soil.

3.2. Content of the EDTA-soluble HM

Zinc. From hydromorphic Technosols at natural humidity, the EDTA solution can dissolve as much as 38–53% of the bulk Zn content, but extractability of this metal decreases to 36–37% after the oil drying for 1 month (Table 2).

In Vertisols at natural humidity, EDTA dissolves 60% of the bulk Zn content. After the sample drying for 1 month, extractability of this metal decreases to 45% and is retained after storage for 3 years 47%.

Kinetics of the extraction of Zn by the EDTA solution is only influenced by the moisture content during the first month of sample storage. A drastic change of redox conditions appreciably decreases the Zn dissolution. However, a further insignificant decrease of the water content in soil samples does not influence the extractability of this metal.

Lead. In hydromorphic Technisols at natural humidity, EDTA dissolves 29–44% of the bulk Pb content. The extractability of Pb decreases to 28–36% after the sample drying for 1 month and to 24–29% after storage for 3 years (Table 2).

In hydromorphic Vertisols, EDTA dissolves 48% of the bulk Pb content. After drying for 1 month and storage for 3 years, extractability of this metal decreases to 31 and 25%, respectively.

Copper. From hydromorphic Technosols at natural humidity, EDTA can extract 2–6% of the bulk Cu content. The extractability of this metal decreases to 2–4% after storage for 1 month and to 1–2.5% after storage for 3 years (Table 2).

In hydromorphic Vertisols at natural humidity, EDTA dissolves 9.6% of the bulk Cu content. The extractability of this metal decreases to 7% after drying for 1 month and to 5.9% after storage for 3 years.

3.3. Content of the oxalate-soluble HM-siderophiles

Zinc. From hydromorphic Technosols at natural humidity, the Tamm reagent extracts 46–54% of the bulk Zn content. The extractability of these metals decreases to 40–42% after the sample drying for 1 month and to 38% after storage for 3 years (Table 2).

In Vertisols at natural humidity, the Tamm reagent dissolves 72% of the bulk Zn. The extractability of this metal decreases to 61% after the sample storage for 1 month and to 53% after storage for 3 years.

Lead. In hydromorphic Technisols at natural humidity, the oxalate dissolves 39–49% of the bulk Pb. The extractability of this metal decreases to 33–40 and 32–35%, respectively, after the sample storage for 1 month and 3 years (Table 2).

From Vertisols at natural humidity, the Tamm reagent extracts 55% of the bulk Pb. The extractability of this metal decreases to 27 and 34%, respectively, after the sample storage for 1 month and 3 years.

Copper. From hydromorphic Technosols at natural humidity, the oxalate extracts 5–9% of the bulk Cu. The extractability of this metal decreases to 4–7 and 3–6%, respectively, after the sample drying for 1 month and its storage for 3 years (Table 2).

In Vertisols at natural humidity, the Tamm reagent dissolves 12% of the bulk Cu. The extractability of this metal decreases to 9 and 8.5%, respectively, after the sample drying for 1 month and its storage for 3 years.

4. Discussion

Application of the mean value obtained with different reagents

Applied Geochemistry 113 (2020) 104493

(Table 2) makes it possible to describe general trends in the HM solubility versus humidity variation in hydromorphic soils.

4.1. Comparison of the HM solubility in wet and dry samples

The content of mobile compounds of Zn, Pb and Cu in hydromorphic soils from the European part of Russia with natural humidity is much higher than in samples stored in the laboratory for 1 month and, particularly, 3 years.

Moreover, extractability of heavy metals from soils is marked by irregular kinetics: solubility of metals decreases rapidly during the first month when the soil sample loses the initial humidity, but slowly during the further storage of the dry sample for 3 years because of the crystallisation of a part of HM compounds. Indeed, when the sample is treated with 1N CH₃COONH₄, the Zn content decreases by 17% (from 43 to 26%) during the first month and only by 2% (mobility of Zn decreases to 24%) after storage for 3 years (Table 2).

Treatment of soils with the EDTA yields similar results. Drastic decrease of the moisture content in the sample during the first month (by 16.1–39.7%) provokes decrease of the mobile Zn content by 11% (from 50 to 39%), whereas the further storage for 3 years storage does not affect its extractability. Analogous kinetics is recorded when Cu is extracted using the EDTA: extractability of metal decreases by 1.6% in the first stage of storage but only by 1.2% in the second stage.

Content of the oxalate-soluble Zn during the first month decreases by 9%. Decrease of the moisture content in the sample by not more than 0.6% after the sample storage for 3 years diminishes the extractability of metal only by 4%.

Impact of oxalate on the dissolution of Pb and Cu is similar. The Pb content decreases by 15% during the first month, but it does not change during the subsequent storage for 3 years. Mobility of Cu during the first month decreases by 2.1% and only by 0.9% after storage for 3 years.

Thus, the long-term storage of dry samples has a small impact on HM mobility, whereas the mobility demonstrates a strong response to the loss of humidity already during the first month of soil drying.

4.2. The difference in the solubility of HM from Technosols and Vertisols

Despite a close position of sectors, hydromorphic Technisols and Vertisols differ strongly in the chemical composition, particularly, in the bulk HM content. In the Technisols, relative to the Vertisols, the bulk content of Zn is 100 times higher, the Pb content is 10–50 times higher, and the Cu content is 3–7 times higher.

However, if soils were compared in terms of the efficiency of HM extraction based on criterion p, the situation turns out to be different. The share of mobile compounds of Cu and, particularly, Zn in all scenarios is higher in the Vertisols. The relative solubility of Cu is higher in the Vertisols in all versions except the impact of 1N CH₃COONH₄. For example, the mean value of criterion p for Zn extracted from the fresh Vertisols is $61.3 \pm 5.8\%$, as opposed to $p = 44.5 \pm 3.9\%$ during the treatment of Technosols. The difference of average values is reliable at probability P = 0.95. This trend is retained in dry samples. After drying for 1 month, the share of the soluble Zn is higher in Vertisols: $p = 37.7 \pm 4.9\%$, as compared to Technisols ($p = 32.8 \pm 9.9\%$). After storage for 3 years, the share of the soluble Zn remains higher in Vertisols ($p = 36.3 \pm 1.7\%$) than in Technisols ($p = 32.0 \pm 4.3\%$).

4.3. The discrepancy in the solubility of different HM

Extraction of heavy metals with different reagents demonstrates the following common series: $Zn > Pb \gg Cu$. The discrepancy is most prominent in the solubility of metals from samples with natural humidity.

For example, in soil samples at natural humidity, irrespective of the applied solvent and soil type, the average value of mobility is as follows: Zn 50%, Pb 38%, and Cu 5%. After storage for 1 month, average values

are as follows: Zn 38%, Pb 27%, and Cu 4%. After storage for 3 years, the values are Zn 36%, Pb 24%, and Cu 3%. Depending on the sample storage duration, discrepancy in the impact of reagents in the series Zn > Pb \gg Cu is as follows: 45% at natural humidity, 34% at the moisture content of 4.4–4.7% (after drying for 1 month), and 33% after storage for 3 years.

Thus, the greatest discrepancy in the efficiency of reagents with respect to the above metals is observed in the case of wet samples.

Based on stability constants (log K), the most mobile HM compounds are dissolved by acetate, whereas the least mobile compounds are dissolved by EDTA (Table 3) (Lur'e, 1988). These constants make it possible at the first approximation to predict the impact of each of the three reagents during the extraction of Zn, Pb and Cu compounds. According to D.S. Orlov (1990), values of log K with fulvic acids at pH = 5 demonstrate the organophilic property of metals: it is maximum for Cu and minimum for Zn (Table 3). Judging from these values, we can assume the following inequality series: $HM_{acetate} < HM_{eDTA}$. Actually, however, such succession is observed not in all soils.

For example, in the Pb-contaminated soils of Indiana (USA), a part of this inequality is observed: $Pb_{dry(oxalate)} < Pb_{dry(EDTA)}$ (Elliott, Herzig, 1999). In the Zn-contaminated soils from Palmerton (USA), the pattern is reversed: at pH = 6–8, $Zn_{dry(oxalate)} > Zn_{dry(EDTA)}$ (Elliott, Shastri, 1999). This can likely be caused by the presence of a greater amount of Zn-siderophiles than Zn-organophiles in this soil.

The difference in the stability of HM compounds affects their extractability. For example, the 1N CH₃COONH₄solution extracts up to 43% of the bulk Zn content from samples at natural humidity and up to 24–26% from the dry samples. However, its efficiency for the Cu dissolution is lowest (<2%) among all reagents (Table 2), although the bond strength of acetate with Zn is minimum (log K = 1.57), as opposed to the bond with Cu (log K_{Cu} = 2.23) and Pb (log K_{Pb} = 2.68) (Table 3). Probably, if the bond strength in metal–acetate complexes is low, small discrepancies instability constants of Cu, Zn and Pb do not play an important role in the extractability of these heavy metals.

The share of the mobile Cu extracted by the 1N CH₃COONH₄solution from the studied soils is very low-even lesser than from the artificially polluted Chestnut and Chernozem soils of the Lower Don valley (Minkina et al., 2008). Such low values suggest high stability of the composition of metal compounds. Since Cu is an organophilic element, it is assumed that the studied soils are dominated by Cu-organic compounds, the bond strength of which promotes both the humate composition of organic matter and the high pH value (\approx 8) in the soil (Minkina et al., 2018c).

4.4. Causes of the efficiency of oxalate as extractant of HM from hydromorphic soils

With respect to the dissolution efficiency of mobile HM compounds in the studied soils, the reagents are arranged in the following series: oxalate > EDTA > CH₃COONH₄. Since the oxalate actively dissolves Fe (II)-compounds in soils (Blesa et al., 1987), the siderophility of heavy metals is determined based on their solubility in oxalate, because siderophility is the main factor governing the mobility of these HM in hydromorphic soils.

The solubility of heavy metals in oxalate depends, first of all, on the mineralogy of Fe. Some minerals are sensitive to the impact of oxalate, while other minerals are insensitive. The group of iron minerals, which

Table 3

Stability constant of Cu, Pb and Zn with organic ligands, log K (Lur'e, 1988) and with fulvic acids (Orlov, 1990).

Metals	Fulvic acid	Acetate	Oxalate	EDTA
Cu	8.69	2.23	6.70	19.7
Zn Pb	2.34 6.13	2.68	4.85 4.90	17.5 19.0

can resist the influence of acid ammonium oxalate, includes the coarsegrained hematite, goethite and many Fe-phyllosilicates. In contrast, response of other hydroxides (ferrihydrite, feroxyhyte, and dispersed goethite) to the oxalate processing depends on the redox conditions in soil during the sampling (Vodyanitskii et al., 2019; Vodyanitskii and Minkina, 2019).

At low E_H values in the water-saturated soils and sediments, the samples are saturated with Fe(II). In this case, treatment of wet samples by ammonium oxalate provokes the reduction of Fe(III) hydroxides (Blesa et al., 1987; Vodyanitskii, 2001). In contrast, the content of non-stable Fe minerals, which are sensitive to the treatment by the ammonium oxalate, decreases after the oxidation of Fe(II) in the course of soil drying. In the dried soil, particles of the non-stable Fe(III) hydroxides are crystallised gradually, resulting in a decrease of the oxalate solubility of compounds of Fe and associated HM-siderophiles.

The studied hydromorphic Technisols are classified as ferruginated soils. The Fe content in hydroxides is as much as 20–30% of the bulk content of this metal and 0.84–1.62% of the bulk content of other chemical elements in soils (Minkina et al., 2018c; Vodyanitskii et al., 2019).

In the studied soils, oxalate demonstrates the best performance in the extraction of Zn (Table 2). In lower beds of the lithosphere, Zn occurs mainly in sulfides. Therefore, geologists assign this metal to the chalcophile group. In autotrophic soils, where sulfides are not retained, Zn often demonstrates the siderophilic property. In hydromorphic soils, the situation is intermediate: Zn occurs in the composition of both oxides and sulfides. For example, in the studied hydromorphic Technisols, the synchrotron X-ray analysis detected compounds with both Zn-O and Zn–S bonds (Minkina et al., 2018a). Precisely pyrite (FeS₂) can provide high efficiency of oxalate as extractant of both Fe (Vodyanitskii, 2001) and associated heavy metals (first of all, Zn) (Table 2). Particularly notable is the predominance of oxalate, relative to other common reducers of Fe hydroxides and/or oxides applied for the sequential fractionation with the hydrochloric hydroxylamine in the acetic acid. From the two studied samples of hydromorphic Technosols, oxalate extracts 1.6 times more Zn than the hydroxylamine chloride (Minkina et al., 2018a).

Lead and zinc in the soils display strong organophilic properties. However, a significant amount of Pb can also be sorbed by iron hydroxide particles (Morin et al., 1999).

5. Conclusions

The content of the mobile compounds of Zn, Pb and Cu in the southern European part of Russia turned out to be much higher in the hydromorphic soil samples with natural humidity than in samples stored for 1 month and, particularly, 3 years. At the same time, kinetics of the extractability of each HM is marked by an irregular pattern: solubility decreases rapidly during the first month when the soil sample loses the initial humidity. The solubility decreases slowly during the further storage of dry sample for 3 years because of the crystallisation of a part of mobile compounds.

In terms of the absolute content, Technosols yielded a greater amount of metals (particularly, Zn and Pb) than Vertisols. However, the share of mobile compounds of Cu (and, particularly, Zn) is higher in Vertisols. The relative efficiency of the impact of "light" reagents upon HM turned out to be lower in Technisols: despite a higher value of the absolute pollution, the share of mobile HM compounds decreases if the hydromorphic soils are strongly contaminated.

The studied reagents (CH₃COONH₄, EDTA and oxalate) demonstrate the following common series: $Zn > Pb \gg Cu$. The discrepancy is most significant for the solubility of metals in wet samples and decreases later in the course of soil sample drying.

In terms of the dissolution efficiency of mobile HM compounds in hydromorphic soils, the extractants are arranged in the following series: $oxalate > EDTA > CH_3COONH_4$. Since the oxalate actively dissolves Fe

(II) compounds in soils, the solubility in oxalate is governed by siderophility of the specified HM. Siderophility is the main factor governing the mobility of a certain HM in the hydromorphic ferruginated soils. Zn is most intensely dissolved by the oxalate. Pb and Cu in soils display the organophilic properties, but Pb can also be associated with iron hydroxides.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Y. Vodyanitskii et al.

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