



Speciation of Zn and Cu in Technosol and evaluation of a sequential extraction procedure using XAS, XRD and SEM–EDX analyses

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Abstract Metal speciation, linked directly to bioaccessibility and lability, is a key to be considered when assessing associated human and environmental health risks originated from anthropogenic activities. To identify the Zn and Cu speciation in the highly contaminated, technogenically transformed soils (Technosol) from the impact zone near the industrial sludge reservoirs of chemical plant (Siverskiy Donets River floodplain, southern Russia), the validity of the BCR sequential extraction procedure using the X-ray

absorption fine-structure and X-ray powder diffraction (XRD) analyses was examined after each of the three stages. After the removal of exchange and carbonate-bonded Zn and Cu compounds from Technosol (first stage of extraction), the resulting residual soil showed enrichment in a great diversity of metal compounds, primarily with Me–S and Me–O bonds. The number of compounds with a higher solubility decreased at the subsequent stages of extraction. In the residual soil left over after extracting the first and second fractions, the dominant Zn–S bond appeared as würtzite (hexagonal ZnS) that made up more than 50%, while the Cu–S bond was almost completely represented only by chalcocite (Cu₂S). The XRD analysis revealed the

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authigenic minerals of metals with S: sphalerite (cubic ZnS), würtzite (hexagonal ZnS), covellite (CuS) and bornite (Cu₅FeS₄). The scanning electron microscopy data confirmed that würtzite was the dominant form of Me with sulfur-containing and carbonate-containing minerals. The Zn–S bond was the main component (57%), whereas the Cu–O bond was dominant in the residual fraction (the fraction after the third-stage extraction). The results revealed that the composition of the residual fractions might include some of the most stable and hard-to-recover metal compounds of technogenic origin. Thus, the application of the novel instrumental methods, coupled with the chemical fractionation, revealed the incomplete selectivity of the extractants in the extraction of Zn and Cu in long-term highly contaminated soils.

Keywords Soil · Zink · Copper · Sequential extraction · Contamination · XRD · XANES · EXAFS · SEM–EDX

Introduction

At present, contamination with heavy metals (HM) is a serious hazard for the environment. There is a delicate balance when metals are vital for biological functioning and when they become potentially hazardous, and their bioaccessibility surpasses the homeostatic control of living organisms (Kabata-Pendias 2011). For example, Cu and Zn, essential microelements, are among the most widespread pollutants in the environment. Recently, great attention is devoted to studying HM behavior in soils due to their ever-increasing pollution due to several anthropogenic activities, such as mining and smelting, irrigation with the HM-rich wastewater and transportation (Rajapaksha et al. 2015). The soils can act as sink and/or source of metals involving potentially harmful effects for human and environmental health (Acosta et al. 2015). At the same time, the degree and trend of biological impact are governed not only by the concentration of metals, but also by their speciation in soils. Speciation is defined as the identification and quantification of different element-finding forms (Tack and Verloo 1995).

The chemical sequential extraction is most widely used for determining the speciation of metals in soils

(Jacquat et al. 2009; Kirpichtchikova et al. 2006; Manceau et al. 2002; Nevidomskaya et al. 2016; Scheinost et al. 2002; Voegelin et al. 2008). This method makes it possible to get information about the association of metals with the geochemical phases in soil and thus provides insight into processes regulating the mobilization of metals and possible ecological risks (Yuan et al. 2004). The main geochemical phases—carriers of HM in soils are represented by clay minerals, amorphous and crystallized Fe–Mn oxides and hydroxides, organic matter and carbonates (Strawn and Baker 2008). Their role in the HM fixation depends on the soil type and strength of the bond with the metal.

There are several sequential extraction procedures for determining HM compounds, and they differ significantly in terms of the composition of extracting solutions and impact upon the soil. A new three-stage sequential extraction method was developed for testing the soil (Ure et al. 1993; Sutherland et al. 2010). In this procedure, metals are divided into the acid-soluble/exchangeable, reducible and oxidizable fractions. Sequential extractions are easily accomplished using accessible chemical reagents (Favorito et al. 2017). However, when working with a complex polydispersed heterogeneous system like soil, these procedures have several disadvantages, such as (1) incomplete selectivity of the extractant, (2) incomplete dissolution of target phases; (3) re-adsorption when an element released during the extraction stage is re-adsorbed onto an undissolved phase and (4) re-precipitation when the released element can further interact with impurities from the extractant (Kirpichtchikova et al. 2006; Leermakers et al. 2019; Scheinost et al. 2002; Sulkowski and Hirner 2006). There is no sequential extraction method which can determine types of the metal bond with the main phases—carriers and eigenphases of metals produced as low-soluble oxides and salts (Scheinost et al. 2002; Minkina et al. 2018, 2019).

Different HM species show unique spectral features that can be used to quantitatively estimate the metal speciation in complex sample matrices by using the linear combination fitting (LCF) with reference spectra from the representative metal compounds. The synchrotron-based X-ray absorption fine structure (XAFS) analyses are noninvasive and element-specific techniques. These methods can probe all of the irradiated HM atoms in a sample and directly

determine their chemical compounds. Most often, analyses of the extended X-ray absorption fine structure (EXAFS) and the X-ray absorption near-edge structure (XANES) are used. The X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for the phase identification of a crystalline phase. These methods have yielded essential information about HM species in soils (Scheinost et al. 2002; Strawn and Baker 2008; Lee et al. 2005; Minkina et al. 2018, 2019).

In the present work, the speciation of Zn and Cu in Technosol was determined based on the results of X-ray absorption spectroscopy (XAS) and XRD after each stage of the sequential extraction procedure using the scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDXS) methods. Together, these approaches would be a more reliable tool for the determination of HM transformations in the highly contaminated soils.

Materials and methods

Studied site and sample collections

The study area is impact territory of the Siverskyi Donets River floodplain (southern Russia) that was used as a wastewater disposal basin for a chemical plant in the 1950s–1990s and now is a dried-up oxbow (Minkina et al. 2018). To study this area, a geochemical grid of 100 monitoring plots was established. The area under study was about 12 hectares. Soil samples were taken according to the procedure described in ISO 10381-1 (2002). The sampling depth varied from 0 to 20 cm. In the present work, one monitoring plot with the highest level of anthropogenic pollution adjacent to the lake was selected (D4) of the overall sampling (Bauer et al. 2018). According to IUSS (2015), anthropogenically transformed soil is classified as Spolic Technosol. The soil at the monitoring plot D0 situated 1200 m away from the lake was used as a background, because there was Fluvisol typical for the area under consideration (IUSS 2015).

Physical and chemical soil analysis

The main physicochemical properties of soil samples (< 2 mm fraction) were determined by the following methods: pH in H₂O using a glass electrode in a 1:5

(volume fraction) suspension of soil in water, ISO 10390 (2005); organic matter content by the sulfochromic oxidation, ISO 14235 (1998); and carbonate content volumetric method, ISO 10693 (1995). The particle size distribution was determined by the pipette method with the pyrophosphate procedure preparation (Shein 2009). The total elemental composition (Si, Al, Fe, Ca, Mg, S, Na) in the soils was determined by X-ray fluorescent (XRF) scanning spectrometer SPECTROSCAN MAK-C-GV.

Sequential extraction procedure

Soil samples were analyzed by the European Community Bureau of Reference—BCR sequential extraction procedure (Ure et al. 1993; Sutherland 2010). The BCR standard procedure allows us to extract metals bound with three fractions: acid-soluble metals bound with carbonates (extraction step 1), reducible metals bound with iron and manganese hydroxides (extraction step 2) and oxidative metals bound with the organic material (extraction step 3). To the three-stage BCR method, a (+ 1) fourth stage was added to obtain a residual fraction soluble by digestion in aqua regia (Table 1). Content of HM in extracts was then quantified by the atomic absorption spectrophotometry (Scientific Buck 200 A, USA).

X-ray absorption spectroscopy and X-ray powder diffraction

After each fractionation stage, residue from one of the replicates was used for the XAFS and XRD analyses. Sufficient replicates were used so that profile triplicates remained for the statistical analysis at the end of extraction. The XAFS spectra were recorded at the Zn and Cu K-edge (9659 eV) using a ‘Structural Materials Science Station’ beamline (Chernyshov et al. 2009) of the Kurchatov Synchrotron Radiation Source (Kurchatov Institute, National Research Center, Moscow, Russia). All spectra were recorded under ambient conditions (23 °C). The beam spot dimension was about 0.5 × 0.5 mm. The radiation intensity was measured using two ion chambers filled with appropriate N₂–Ar mixtures in the energy range varying from 200 to 800 eV below and above the Zn and Cu K-edge absorption. The EXAFS and XANES data were analyzed using the Viper (Klementev 2001) and IFEFFIT 1.2.11 (Newville 2001) data analysis

Table 1 BCR three-stage sequential extraction scheme

Extraction stage and HM fractions	Extracts
First: water-soluble, exchangeable and carbonate bound fraction	Extraction with 0.11 mol/dm ³ of acetic acid for 16 h at 22 ± 5 °C with constant stirring
Second: reducible fraction (iron/manganese oxyhydroxides)	Extraction with 0.1 mol/dm ³ Na ₂ OH·HCl during 16 h with continuous stirring at pH = 2 (with the HNO ₃ input)
Third: oxidizable fraction (organic matter and sulfides)	(1) 2 h in water bath at temperature 85 ± 2 °C, dispersion H ₂ O ₂ at pH = 2 (2) 16 h in water bath at temperature 22 ± 2 °C, continuous stirring, dispersion 1.0 mol/dm ³ NH ₄ OAc(CH ₃ COONH ₄) at pH = 2 (with the HNO ₃ input)
Residual ^a : residual fraction (soluble in oxidative acids)	Includes dispersed metals with a mixture of concentrated hot acids HNO ₃ and HCl

^aDigestion of the residual material is not a specification of the BCR protocol

packages. Linear combination fittings of the near-edge absorption spectra of soil samples were performed using the spectra of several reference compounds. All spectra were normalized, and the atomic background was subtracted from the raw data. The radial pair distribution functions around the metal atoms were obtained by the Fourier transform of the k-weighted EXAFS functions.

X-ray powder diffraction study of the samples was performed at the X-ray structural analysis beamline (Belok/XSA) of Kurchatov Synchrotron Radiation Source (Svetogorov et al. 2020). The wavelength of monochromatic radiation was 0.8 Å (photon energy 15,498 eV). The sample was placed in a cryoloop of 300 µm in size. Diffraction patterns were collected by the 2D Rayonix SX165 detector. The exposure time was 5 min.

Scanning electron microscope (SEM) and energy-dispersive X-ray (EDX) spectroscopy

Microtexture and elemental composition of samples were examined with a VEGA II LMU (Tescan) scanning electron microscope equipped with INCA Energy 450/XT (Silicon Drift detector, SDD) and INCA Wave 700 (crystals: LiF, PET, TAP, LSM60, LSM200) EDS systems. The INCA Energy + software package makes it possible to exploit both systems simultaneously. The SEM images were obtained using the BSE detector.

Quality control of analysis

The analytical sequential extraction results were validated by the analysis of the certified reference material BCR-701 Sediment. To ensure the quality of results, the reference certified for extractable metal contents in three stages of the BCR sequential extraction procedure and the indicative values for aqua regia extraction (Pueyo et al. 2001) were used. The obtained results and the certified values for this material are given in Table 2. In all cases, we obtained results comparable with the certified values, suggesting the excellent quality of the results. Recovery for the analytes was between 95 and 103%. Moreover, the sum of fraction is comparable with the metal concentration obtained with the aqua regia, ensuring the high quality of analytical extraction data.

Quality control of the X-ray absorption spectroscopy methods included the following procedures: (1) for statistical method for each point in the spectrum, the exposure time of 60 s was taken; (2) for every sample, three spectra were statistically averaged for determining the final spectrum to achieve a higher signal-to-noise ratio; and (3) for the X-ray powder diffraction analysis, each of the studied sample fractions was examined in three replications to scrutinize homogeneity of the fraction composition.

Statistical analysis

The results were analyzed with the Statistica 10.0 statistical functions. We used variation statistics methods to calculate the arithmetic mean and standard

Table 2 Quality control of sequential extraction data using the certified reference material BCR-701

Reference material	First stage	Second stage	Third stage	Residue	Sum of three stages plus residue	Aqua regia extractable content
<i>Zn</i>						
Certified value	205 ± 6.0 ^a	114.0 ± 5.0	45.7 ± 4.0	94.6 ± 12.2 ^b	459 ± 15 ^b	454 ± 19 ^b
Obtained value	200 ± 9.3	111.4 ± 5.2	44.9 ± 3.1	96.5 ± 8.7	452.7 ± 12.6	467 ± 26
Recovery, %	98	98	98	102	99	103
<i>Cu</i>						
Certified value	49.3 ± 1.7	124.0 ± 3.0	55.2 ± 4	38.5 ± 1.2 ^b	267 ± 12 ^b	275 ± 13 ^b
Obtained value	47.5 ± 1.3	120.7 ± 2.7	52.4 ± 3.1	36.9 ± 1.7	258.8 ± 11.3	262 ± 9
Recovery, %	96	97	95	96	97	95

^aMean ± SD, mg kg⁻¹; n = 3

^bIndicative values

deviation of three determinations. Statistically significant differences between the means were determined by Fisher’s least significant difference (LSD) test and were accepted as valid at a significance level of $p \leq 0.05$.

Results and discussion

Properties of soil samples

In the uncontaminated Fluvisol (D0), the organic matter (OM) content is $3.4 \pm 0.1\%$ at $\text{pH } 7.3 \pm 0.2$ with insignificant carbonates ($1.3 \pm 0.02\%$). The OM content in Technosol (D4) is $4.4 \pm 0.2\%$. The pH is mild basic (7.7 ± 0.1). The CaCO_3 content in the polluted soil ($5.3 \pm 0.3\%$) is four times higher than in Fluvisol. In soil from plot D0, the content of the physical clay fraction and clay particles is $53.1 \pm 2.7\%$ and $32.4 \pm 2.1\%$, respectively. Soil from plot D4 has analogous contents of these fractions: 52.1 ± 3.8 and $33.0 \pm 2.6\%$, respectively.

Major elements determined in Fluvisol were Si (62.8% SiO_2), Al (14.7% Al_2O_3) and Fe (7.5% Fe_2O_3), with minor contributions from Ca (3.2% CaO), Mg (1.5% MgO), Na (1.0% Na_2O) and S (0.03% SO_3). The composition of Technosol was significantly higher in Fe (11.7% Fe_2O_3), S (7.3% SO_3) and insignificantly lower in Si (54.8% SiO_2), Al (11.8% Al_2O_3), Fe (6.0% Fe_2O_3) compared to uncontaminated Fluvisol. The contents of Zn and Cu in Fluvisol from plot D0 are 90 and 44 mg/kg, respectively, which

differ insignificantly from the Clarke values (Vino-gradov 1957). Technosol is marked by polyelement pollution, with notably higher average Zn and Cu contents relative to the Clarke value: Zn (hundreds of times higher), Cu (several times higher). Zinc is the primary pollutant in the studied Technosol. Its content in the soil is 62032 mg/kg, i.e., more than 6.2 wt%. Copper content in the soil of contaminated area is 147 mg/kg.

Speciation of metals based on the sequential extraction

In the uncontaminated soil (plot D0), Zn and Cu prevail notably in the residual fraction (61 and 85%, respectively, of the bulk content) (Table 3). Metal mobility in the Fluvisol is low. The HM content in the first stage characterized by the weakest bond with soil is just 1% for Cu and 7% for Zn. Discrepancies in the share of separate fractions from the total content of the respective element are caused by different affinities of metals to the soil components: the reducible fraction is marked by high Zn content; the oxidizable fraction, by high Cu content. In the background soil, low mobility and domination of metal in the residual fraction are established which indicates the absence of technogenic metal contamination.

In soil from the monitoring plot D4 adjacent to Lake Atamanskoe, the entire content of metals increases in all fractions (Table 3). The distribution pattern of HM associated with different fractions in Technosol is as follows:

Table 3 Fraction composition of Zn and Cu compounds in Fluvisol (D0) and Technosol (D4) near the industrial sludge reservoirs of chemical plant (Lake Atamanskoe area, Siverskiy Donets River floodplain, southern Russia)

Monitoring plot	Fractionation stage			
	First	Second	Third	Residual
<i>Zn (mg/kg)</i>				
D0	6.0 ± 0.04	15.0 ± 1.2	13.8 ± 0.7	55.2 ± 7.2
D4	11,720 ± 106	29,954 ± 2356	2794 ± 146	17,559 ± 1491
<i>% Of the sum of fraction</i>				
D0	7	17	15	61
D4	19	48	5	28
<i>Cu (mg/kg)</i>				
D0	0.6 ± 0.1	1.6 ± 0.1	4.4 ± 0.6	37.1 ± 2.8
D4	18.0 ± 0.9	12.0 ± 1.0	34.1 ± 3.7	82.8 ± 9.1
<i>% Of the sum of fraction</i>				
D0	1	4	10	85
D4	12	8	23	56

Zn: Reducible > residual > acid – soluble > oxidisable

Cu: Residual > oxidisable > acid – soluble > reducible

Fractionation of Zn in the technogenic soil unraveled a high degree of metal fixation with Fe–Mn (hydr)oxides, confirming the data reported in (Fernández-Ondoño et al. 2017; Marguá et al. 2007; Nannoni et al. 2011). The fraction associated with Fe oxides is high due to the presence of a large amount of Fe oxides in studied soil (60 g/kg) and their fixing capacity (Covelo et al. 2008). This agreement can be related to the following fact: equilibrium constants of Fe–Mn oxides and hydroxides are sufficiently high for concentrations of Zn phases in this fraction (Mahanta and Bhattacharyya 2011; Ramos et al. 1994). According to NIST Standard Reference Database 46, critically selected stability constants of metal complexes for the equilibria are as follows: $\text{SOH} + \text{Zn}^{2+} \rightleftharpoons \text{SOZn}^+ + \text{H}^+$.

Equilibrium constants (log K) are as follows: 0.99 and – 2.9 (Fe hydroxides), – 0.96 (Al hydroxides), – 0.01 (Mn hydroxide). Previous studies of Technosol with the Mössbauer spectroscopy and scanning electron microscopy revealed a significant share of Zn in iron compounds (Vodyanitskii et al. 2019). The studied Technosol includes hydrogoethite (with a high content of the absorbed water), rare mineral schwertmannite, oxidized Zn-rich magnetite, wüstite particles and siderite with a partial displacement of Fe^{2+} by Zn^{2+} .

In terms of the relative and absolute content, the next (after the reducible variety) is the residual

fraction. According to the data obtained after the chemical sequential chemical, Zn in the latter fraction is confined mainly to silicates. However, the share of this Zn fraction in soil from plot D4 located near the former lake falls to 33%, relative to the background soil in a plot located away from the pollution source (Table 3). Analogous trends of reverse correlation between the most conservative residual Zn fraction and the technogenic pollution of soils are also reported in Burachevskaya et al. (2019) and Nielsen et al. (2015).

In the Zn-contaminated soil (D4), the relative decrease of metal in the one fraction associated with phyllosilicates is accompanied by a simultaneous increase in the most mobile acid-soluble fraction including the exchange and specifically absorbed metal compounds. Similar trends were reported in Ghayoraneh and Qishlaqi (2017), according to which Zn shows relatively high mobility in Technosol, making Zn more mobile than Cu. Similar BCR fractionation studies showed that Zn was abundant in the unstable form bounded to carbonates in the contaminated river sediments (Akçay et al. 2003; Vieira et al. 2009).

The share of the OM-associated fraction accounts for 5% of metal in Technosol (Table 3). Zinc is marked by a weak capacity to make up robust chelate complexes with organic compounds. At high OM content in the soil, metalloorganic complexes (primarily, metals-organophilic) are formed (Pinskii and Minkina 2013). This is suggested by stability constants of metal complexes with humic acids (Kabata-

Pendias 2011). At pH 7, the stability constant of Zn with humic acids is 10.3. For Cu marked by a high organophilic potential, the value is 12.3.

More than one-half of Cu (56%) examined in Technosol was detected in the residual fraction, meaning that this metal was strongly bound to the soil. Accumulation of the imported metal compounds in crystal lattices of clay minerals was a prolonged process, but it dominated because of the prolonged pollution period (more than 60 years). The EXAFS analysis revealed that Cu^{2+} cations absorbed by the soil can replace a part of Al^{3+} ions at octahedral sites of clay minerals (Minkina et al. 2013). This explains the high percentages of Cu in the residual fraction reported in our work and previous studies (Al-Hwaiti et al. 2015).

At a high Cu content in soil (D4), the main absorber of metal is OM, and the oxidizable fraction accounts for 23% (Table 3). The significant share of Cu identified in the oxidizable Technosol fraction is related to a rather high OM content (average 4.4%). Copper is also characterized by a high complex constant with OM as it forms strong associations with oxygen and sulfur atoms on the OM surface (Cuong and Obbard 2006; Xia et al. 1997). The Cu content in the first stage is lower than in the residual and oxidizable fractions. It makes up 12% of the bulk metal content in the soil. This fact is attributable to the soluble complexes that OM can form with Cu, and they contribute more to the exchangeable fraction. Although Cu was able to be adsorbed at higher levels than the other metals, the mobility of this metal could have increased due to the high affinity of the soluble organic ligands to the Cu^{2+} ion (McLean and Bledsoe 1992). The reducible fraction associated with Fe–Mn (hydr)oxides is lowest (not more than 8%) in the studied contaminated soil (Table 3).

Speciation of metals based on the instrumental methods

Synchrotron X-ray diffractograms of soil samples taken from Technosol after the BCR selective extraction (Fig. 1a–c) revealed the following: soil sample after the third extraction stage turned out to be most homogeneous in terms of the composition of crystalline mineral phases, as suggested by the almost complete coincidence between the diffractograms of

all three replications. Diffractograms of soil samples after the second stage show variations in the intensity of some maxima, indicating the heterogeneity and different contents of some mineral components. The highest discrepancies in the intensity of separate maxima were detected in diffractograms of soil sample after the first stage. This sample demonstrated individual diffraction peaks that were undetected in samples of other fractions.

During the analysis of each reflection in X-ray diffractograms, Bragg angles and corresponding interplanar distances were determined (Supplementary material). Diffraction peaks corresponding to mineral components in each of the studied fractions were defined. Quartz is among the dominant components in soil samples after different extraction stages. However, the fractions differ in terms of the composition of other minerals. In addition to diffraction peaks corresponding to quartz, five sufficiently weak diffraction maxima were also observed in soil samples after different stages. At the same time, the majority of peaks occur in diffractograms of soil samples after the first and second stages. In particular, X-ray diffractograms of samples of the fraction after the first and second stages include intense peaks corresponding to würtzite (hexagonal ZnS) (Fig. 1a, b). However, the presence of other sulfur-containing metal compounds such as sphalerite (cubic ZnS), covellite (CuS) and bornite (Cu_5FeS_4) cannot be ruled out.

The diffractograms also show other metal compounds with sulfur: sphalerite (cubic ZnS), covellite (CuS) and bornite (Cu_5FeS_4). Soil samples differ particularly strongly in terms of the content of mineral phase würtzite. Soil after the first stage is most saturated with sulfides, whereas crystalline sulfides are lacking and phyllosilicates are dominant in the fraction after the third stage (Table, Supplementary material).

The sensitivity of the near-edge XANES spectra to the bond geometry can be used for a preliminary qualitative analysis of the Zn surrounding samples of three fractionation stages. The Zn K-edge XANES spectra of the reference Zn-containing compounds with known Zn–S (ZnS) and Zn–O bonds (ZnO and ZnSO_4) demonstrate a significant discrepancy in the position of absorption edge, making it possible to discriminate different types of the Zn surrounding in Technosol samples.

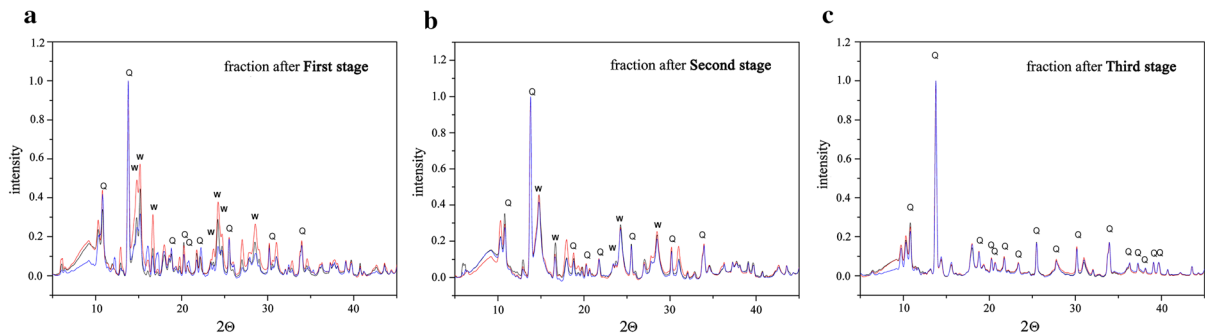


Fig. 1 Mineral components in synchrotron X-ray diffractograms of Technosol samples after the BCR selective sequential extraction

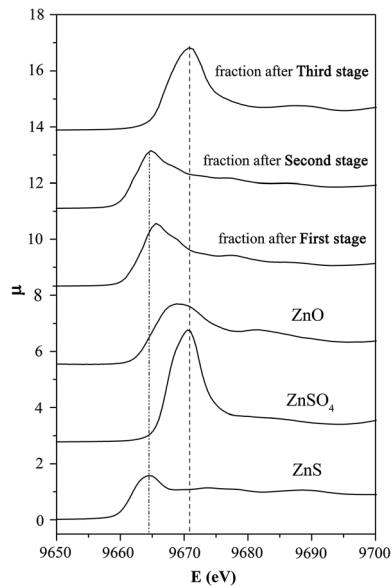


Fig. 2 Zn K-edge XANES spectra of fractions extracted from Technosol samples after the selective extractions and of reference samples

As seen in Fig. 2, the Zn K-edge XANES spectrum of soil sample after the third extraction stage demonstrates similarity with reference spectra, in which Zn is coordinated with oxygen (ZnO, ZnSO₄), and the main absorption peak is located at ~ 9670 eV. The XANES spectrum of soil samples after the first and second stages is close to that of ZnS, where the main absorption peak is located at ~ 9665 eV. However, it also demonstrates higher energy features, suggesting the possibility of mixed Zn–S and Zn–O bonds in Technosol samples.

Figures 2 and 3 present the Zn K-edge EXAFS spectra in the k and R space for soil samples after different stages, as compared to reference compounds

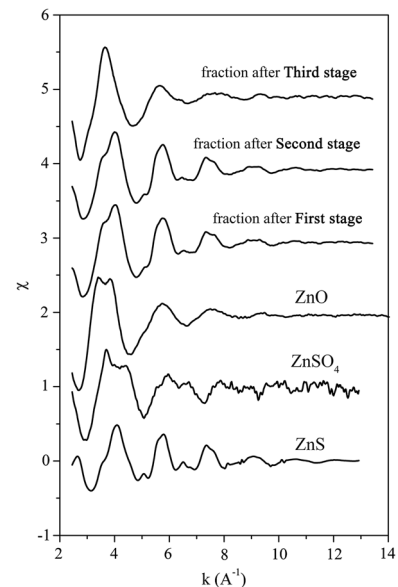


Fig. 3 k^2 -weighted EXAFS oscillations in the Zn K-edge absorption spectra of fractions extracted from Technosol samples after the selective extractions and of reference samples

ZnSO₄, wurtzite (ZnS) and zincite (ZnO). In zincite, Zn atoms are tetrahedrally bonded with O atoms (first coordination sphere) with an average bond length of 1.98 Å. In addition, Zn atoms are surrounded by 12 adjacent Zn atoms at an averaged distance of 3.23 Å (Albertsson et al. 1989). Thus, two peaks observed at the radial distribution function for zincite (ZnO) at 1.5 Å and 2.9 Å (Fig. 3) correspond to distances of Zn–O and Zn–Zn, respectively. In ZnSO₄, Zn is coordinated by four O atoms and only two Zn atoms. The Zn–Zn distance is 3.36 Å, and there are two different short Zn–O bonds (1.95 and 2.04 Å). The spectrum of ZnSO₄, like that of ZnO, contains the Zn–O peak, but the second Zn–Zn peak is virtually

missing because of the low coordination number. The Zn–S bond (2.34 Å in ZnS) is 0.2–0.3 Å longer than the Zn–O bond in ZnO and ZnSO₄. Therefore, the peak corresponding to Zn–S is observed in the Fourier transform (FT) of EXAFS at a greater distance (Fig. 4). This obvious discrepancy makes it possible to identify the Zn–S and Zn–O bonds in Technosol.

Like the XANES version, the Zn K-edge FT EXAFS spectra of sample fractions demonstrate explicit differences, suggesting that metal species in these samples are different. After the third fractionation stage, the remaining soil fraction is defined as the fraction connected with silicates. Thus, this fraction was represented by phyllosilicate minerals in the XANES analysis. The FT EXAFS spectra of the soil sample after the third stage show the closest similarity with the analogous spectrum of ZnSO₄, confirming the results of the analysis of the neighbor structure of absorption spectra. The lack of peak corresponding to the second coordination sphere (Zn–Zn) indicates that ZnO is not the predominant component in the sample. In soil samples after the first and second stages, the main peaks in the FT EXAFS spectra are shifted to the region with greater *R* values (Fig. 4), suggesting that Zn–S bonds can be present in this sample in accordance with the results of XANES analysis.

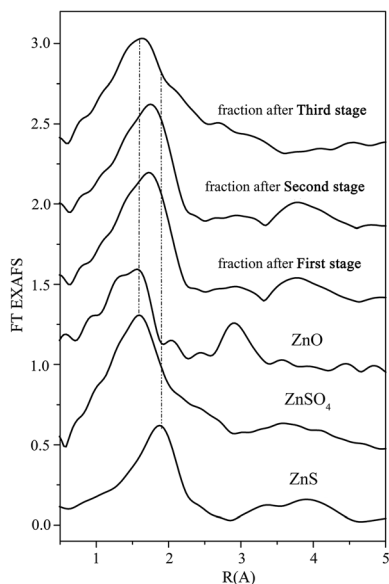


Fig. 4 Best fits of the Fourier transform of Zn EXAFS spectra of Technosol samples after the selective extractions and of reference samples

Based on the assumption that Technosol samples after the fractionation contain Zn–S and Zn–O phases, we accomplished more precise quantitative estimates by adjusting the near-edge spectrum zone using the linear combination of reference compound spectra (Table 4). The results showed that the main differences between the fractions are related to the ZnSO₄/ZnO ratio. Zinc sulfate is the primary component (65%) in fraction after the first stage, in agreement with the predominance of the Zn–O bond in the first shell based on the EXAFS data.

A high level of agreement between the linear combined spectra and experimental spectra from samples of the studied soil fractions suggests that ZnS is appreciable in all samples. In the same time, soils after the second and third stages contain the Zn–S bond (57% and 50%, respectively) as wurtzite (ZnS). According to the results obtained for the upper horizon of the highly contaminated soils in Palmerton (USA), Zn is fixed mainly in sphalerite (ZnS) (Scheinost et al. 2002). Modeling of the experimental Zn K-edge XANES spectra of Technosol samples after the second and third stages revealed the presence of ZnO. According to Voegelin et al. (2005), if the soil is contaminated with zincite (ZnO), the mineral is transformed and incorporated mainly in the Zn-containing trioctahedral structures.

Our previous studies of Technosol using the Mössbauer spectroscopy (Minkina et al. 2018) revealed that hydromorphic conditions and the technogenic pattern of soil formation fostered the appearance of Zn siderophile when this metal is enriched with the Fe-containing oxides and/or hydroxides mainly represented by magnetite and hydrogoethite. The alkaline pH and sufficient quantity of carbonates in the hydromorphic Technosol made it possible to identify

Table 4 Results of the modeling of experimental Zn K-edge XANES spectra of Technosol samples after different stages of the sequential fractionation and linear combinations of the spectra of reference compounds, % of the share of compounds in sample

Fractionation stage	ZnSO ₄	ZnO	ZnS
First	65	0	35
Second	0	50	50
Third	25	18	57

the iron carbonate as siderite (FeCO_3) (Minkina et al. 2019), in which Fe^{2+} is replaced partly by Zn^{2+} . Such processes were reported as well by other researchers (Jacquat et al. 2009; Manceau et al. 2002; Panfili et al. 2005; Schlegel et al. 2001). The results demonstrated that the specific sorption of Zn by the Fe-containing (hydr)oxides, carbonates and phyllosilicates is increased notably under alkaline conditions in the highly contaminated soils.

The type of atoms incorporated in the immediate surrounding of Cu atoms in sample fractions after the selective extractions was determined based on the Cu K-edge XANES spectra (Fig. 5). Reference samples were represented by several Cu-containing compounds, in which the nearest coordination spheres of Cu atoms are composed of O atoms ($\text{Cu}(\text{CH}_3\text{COO})_2$, CuCO_3 and CuSO_4), as well as S atoms (CuS , Cu_2S). In CuSO_4 , Cu is coordinated by four O atoms with two short and two long Cu–O bonds (1.91 and 2.05 Å), and the next coordination sphere with a radius of 2.37 Å has two additional O atoms. In $\text{Cu}(\text{CH}_3\text{COO})_2$, Cu also occurs in the tetrahedral oxygen surrounding, with the Cu–O bond varying from 1.90 to 2.05 Å. In Cu_2S , Cu atoms are coordinated by three S atoms, and the nearest Cu–S distance is 2.29 Å. In CuS , radius of the first coordination sphere composed of three S atoms is 2.17 Å. The significant difference in the position of the absorption edge and main spectral features in samples with the Cu–S and Cu–O bonds

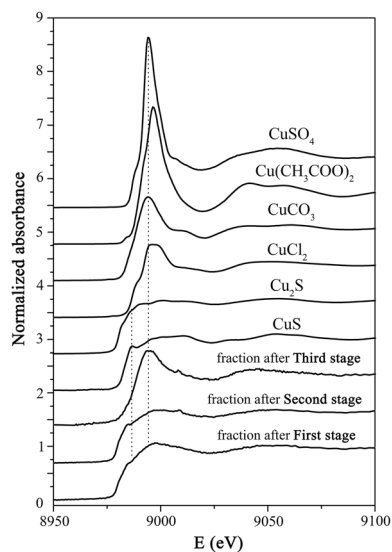


Fig. 5 Cu K-edge XANES spectra of Technosol samples after the selective extractions and of reference compounds

allows us to discriminate reliably these types of the Cu surrounding in the studied sample fractions (Fig. 6).

The Cu K-edge XANES spectrum of Technosol samples after the first and second stages is very similar to that of the Cu-containing sulfur compounds (CuS and Cu_2S), testifying to the abundance of Cu–S bonds. This is additionally supported by the radial atom distribution pattern based on the FT EXAFS spectra (Fig. 6). The Cu K-edge XANES spectrum of fraction after the third stage shows a prominent maximum, which is typical of the spectra from reference samples with the oxygen surrounding Cu. Prevalence of Cu–O bonds in the fraction after the third stage demonstrates a similar position of the absorption edge relative to reference compounds.

In samples with the oxygen surrounding of Cu atoms, the position of peaks of the first coordination sphere is shifted toward the lesser values relative to the sample, in which Cu is coordinated by S atoms. Peaks in the FT EXAFS spectra, which correspond to the first coordination sphere in the fraction after the third stage, have less R values than analogous peaks observed in the FT EXAFS spectra of fractions after the first and second stages.

By adjusting the spectra of the studied Technosol samples based on the linear combination of spectra of the reference compounds, we assessed the

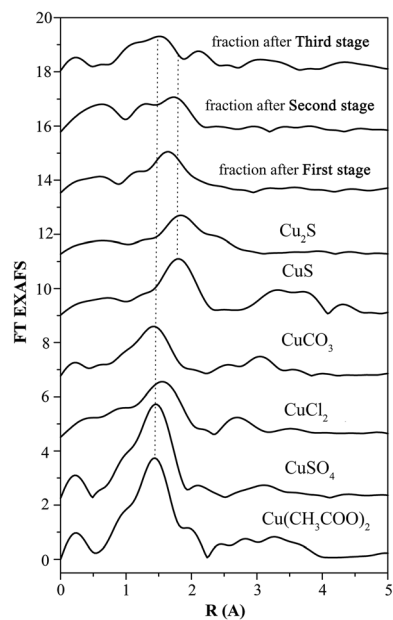


Fig. 6 Fourier transforms of Cu K-edge EXAFS spectra of Technosol samples after the selective extraction

contribution of different materials (Table 5) in the given fractions. The respective spectra and curves obtained after this adjustment are shown in Fig. 7. The results show that samples after the first stage are typically dominated by Cu_2S and CuCO_3 , but they contain a small admixture of CuSO_4 and CuCl_2 . Spectra of soil samples after the second stage match the Cu_2S spectra with a high degree of accuracy, suggesting the prevalence of chalcocite in the given fraction. The soil sample after the third stage is characterized by a high content of CuCO_3 (50% of all Cu compounds) and Cu_2S (30% of all Cu compounds) and a minor admixture of CuSO_4 (12% of all Cu compounds). The residual fraction of contaminated soil might contain some of the most stable and hard-to-recover HM compounds of technogenic origin (Ladonin 2016). Modeling the spectra with a linear combination could not show CuCO_3 compound in the samples of the first and second fractions due to their small amount.

Results of the SEM–EDX analysis of Technosol samples confirmed the presence of Zn and Cu compounds and their concentrations. Zinc compounds are represented by aqueous sulfates associated with gypsum and calcite (Fig. 8a). The EDX spectra revealed that metal concentrations are higher than the detection limit of ~ 0.05 wt% (Fig. 8b). Zinc speciation occurs as ‘crusts,’ aggregates with calcite and gypsum (Fig. 8c), occasional botryoidal aggregates (10–20 μm) or admixture in carbonates (Fig. 8d). The main concentrator of the Zn phase is represented by the aqueous sulfate, goslarite ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) produced after the oxidation of zinc sulfate and wurtzite (ZnS). It has been established that Zn can make up both eigenphases and bonds with clay minerals or carbonates. The latter tend to adsorb Zn

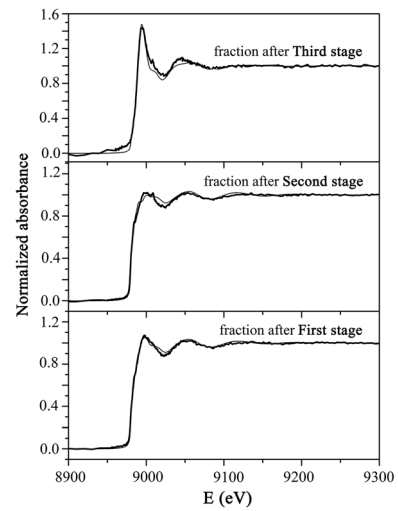


Fig. 7 Experimental Cu K-edge XANES spectra of Technosol samples after the selective extractions (bold line) and linear combination of the reference compound spectra (thin line)

actively and fix it on the surface. High Cu concentration (> 0.05 wt%) (Fig. 8e) was recorded only in the bond with clay aggregates (Fig. 8f).

Conclusions

Detailed knowledge of the molecular-level speciation of HM is required for efficient and cost-effective remediation of soil. Zinc and Cu speciation in the highly contaminated Technosol was studied based on the XAFS and XRD analyses after each stage of the extraction. The combined use of the three-stage BCR procedure coupled with XAFS and XRD could assist us not only to obtain a more accurate determination of the metal speciation in the soils, but also to better understand the complicated and dynamic molecular-level processes of metal assimilation during the technogenic soil formation.

Study of speciation revealed a difference between Zn and Cu. Fractionation of Zn in the technogenic soil unraveled a high degree of metal fixation with Fe–Mn (hydr)oxides and silicates. Hydromorphic conditions and the technogenic pattern of soil formation foster the appearance of Zn siderophile. Cu is characterized by the accumulation in the residual and oxidisable fractions. According to the results obtained in this study, Zn shows a relatively high mobility in Technosol, making it more mobile than Cu. Application of

Table 5 Results of the modeling of experimental Cu K-edge XANES spectra of Technosol fractions at different stages of the selective sequential extraction with the linear combination of reference compound spectra, % of the share of compounds in sample

Fractionation stage	CuSO_4	CuCO_3	Cu_2S	CuS	CuCl_2
First	4	0	86	0	10
Second	0	0	100	0	0
Third	12	50	33	0	0

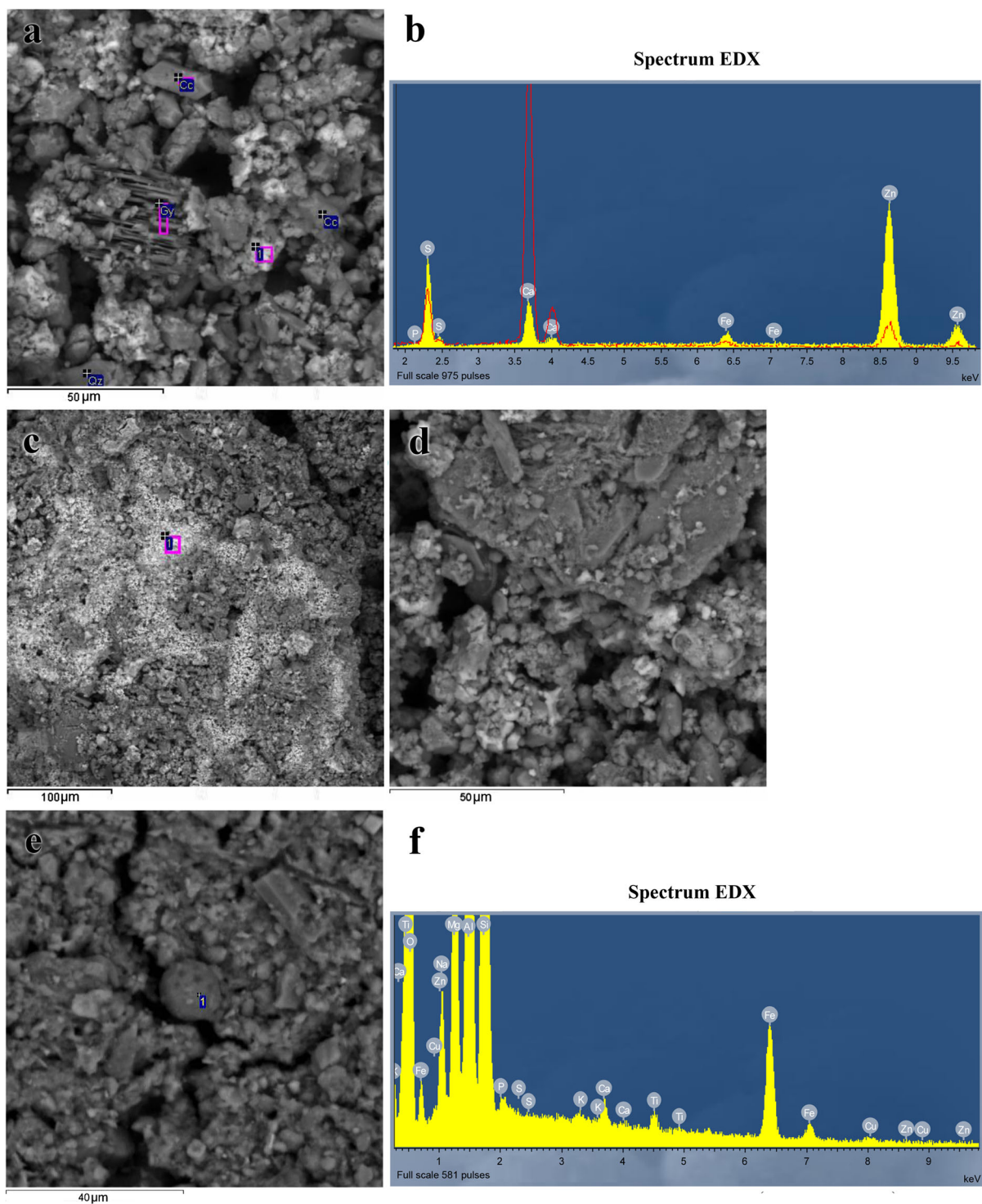


Fig. 8 SEM images of the newly formed minerals of Zn (**a**, **c**, **d**) and Cu (**e**) along with EDX spectra (**b**, **f**)

the linear combination of the XANES and EXAFS spectra after each fractionation stage of Zn and Cu

from the highly contaminated Technosol refined the identification of metal speciation significantly. The

considerable discrepancy in the position of absorption edge and values of the main spectral features in samples with Cu–S and Cu–O bonds makes it possible to discriminate reliably these types of the Cu surrounding in the extracted fractions. The most considerable differences in the intensity of separate maxima were revealed between the diffractograms of soil sample after the first stage. After extracting the first and second fractions from Technosol, the transformation from O-coordinated Zn to S-coordinated Zn associated with minerals was observed. Modeling of spectra by the linear combination of metal-containing compounds revealed the presence of ZnS as the mineral phase würtzite (Cu₂S), as well as compounds ZnSO₄, CuSO₄, CuCO₃ and CuCl₂. The XRD analysis unraveled the presence of authigenic S-containing minerals: sphalerite (cubic ZnS), würtzite (hexagonal ZnS), covellite (CuS) and bornite (Cu₅FeS₄). The SEM–EDX data confirmed that the dominant form of Zn with S is represented by würtzite, while Cu is only recorded in the bond with clay aggregates.

Thus, a combination of various modern analytical methods made it possible to define the main trends of Zn and Cu speciation in the highly contaminated soils during a prolonged chemical impact under hydromorphic conditions. It is shown that extracts used in the BCR method are not entirely selective and they do not provide a complete extraction of metals at all extraction stages. Knowledge of HM speciation in Technosol gained by the physiochemical fractionation procedures coupled with the spectroscopic methods can provide invaluable information about the potential bioavailability of metal species.

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