Molecular characterization of Zn in Technosols using X-ray absorption spectroscopy

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A B S T R A C T

The bioavailability of heavy metals in the soil is a function of their speciation. The speciation of Zn in Technosols of anthropogenic anomalies in Southern Urals and Southern Russia was studied using X-ray absorption spectroscopy and X-ray diffraction methods based on synchrotron radiation. The studied Technosols are characterized by exceedings of the lithosphere clark for Zn in hundreds of times. Hypergenic changes in the mineral composition of Technosols revealed different types of Zn surrounding. In the Southern Ural soils, six oxygen atoms forming a deformed octahedron coordinate Zn. For contaminated Technosols of Southern Russia, the longs of the Zn–O bonds were determined, which are close to the bonds in $ZnSO_4$, and the mixed version of local surrounding with Zn–S and Zn–O bonds. Studies of metal speciation are of extreme importance for revealing the main mechanisms responsible for the mobility of trace elements such as Zn and understanding its consequences in terms of long-term potential emission by the Technosols.

1. Introduction

The development of industrial production provokes significant transformations of ecosystem components. The active growth of industry in Russia in the 20th century resulted in the creation of large industrial centers for the extraction and processing of mineral resources (Chernen'kova, 2002; Gashkina et al., 2015; Kalabin and Moiseenko, 2011; Makunina, 2001; Udachin et al., 2003). Large amounts of solid and liquid waste are accumulated in the form of tailing dumps, technogenic lakes receiving industrial discharges, sludge collectors, etc. (Hu et al., 2006; Juillot et al., 2003; Manceau et al., 2002; Scheinost et al., 2002). Aggressive weathering products (i.e., sulfuric acid, sulfide, sulfates, sulfites, etc.) form in soils with time. The aggressive nature of newly forming compounds with respect to most minerals results in an intensive acid hydrolysis, leaching, and solubilization of large amounts of macro- and microelements. This is accompanied by the disturbance of properties of natural soils and soil cover and favors the development of anthropogenically transformed soils and soil-like formations: Technosols (IUSS Working Group WRB, 2015). Technosols are of special

interest, because structural changes touching the solid phase occur under the long-term contamination, which affects the speciation, mobility, and bioavailability of pollutants (Coussy et al., 2017; Roberts et al., 2002; Root et al., 2015; Van Damme et al., 2010; Voegelin et al., 2005). Technosols are subject to the same factors of soil formation as soils derived from bedrock (climate, organisms, parent material, relief and time) but weather rapidly due to their extreme geochemical, mineralogical, and physical properties, which places them far from equilibrium with earth surface environments (Santini and Fey, 2016). In natural soils, soil-forming processes occur over millenaries and include the formation of specific soil substances like humus (or soil organic matter), as well as the formation, dissolution, and/or precipitation of minerals, according to classical works (Targulian and Sokolova, 1996). In Technosols, the transformations of soil material are strongly accelerated because of thermodynamic misbalances arising from oxidation, carbonization, precipitation of secondary minerals, and other processes (Sparks, 1999; Sposito, 1984, 1989). It is therefore possible to observe soil formation over relatively short (< 100 years) timescales compared to soils derived from bedrock parent materials, with A
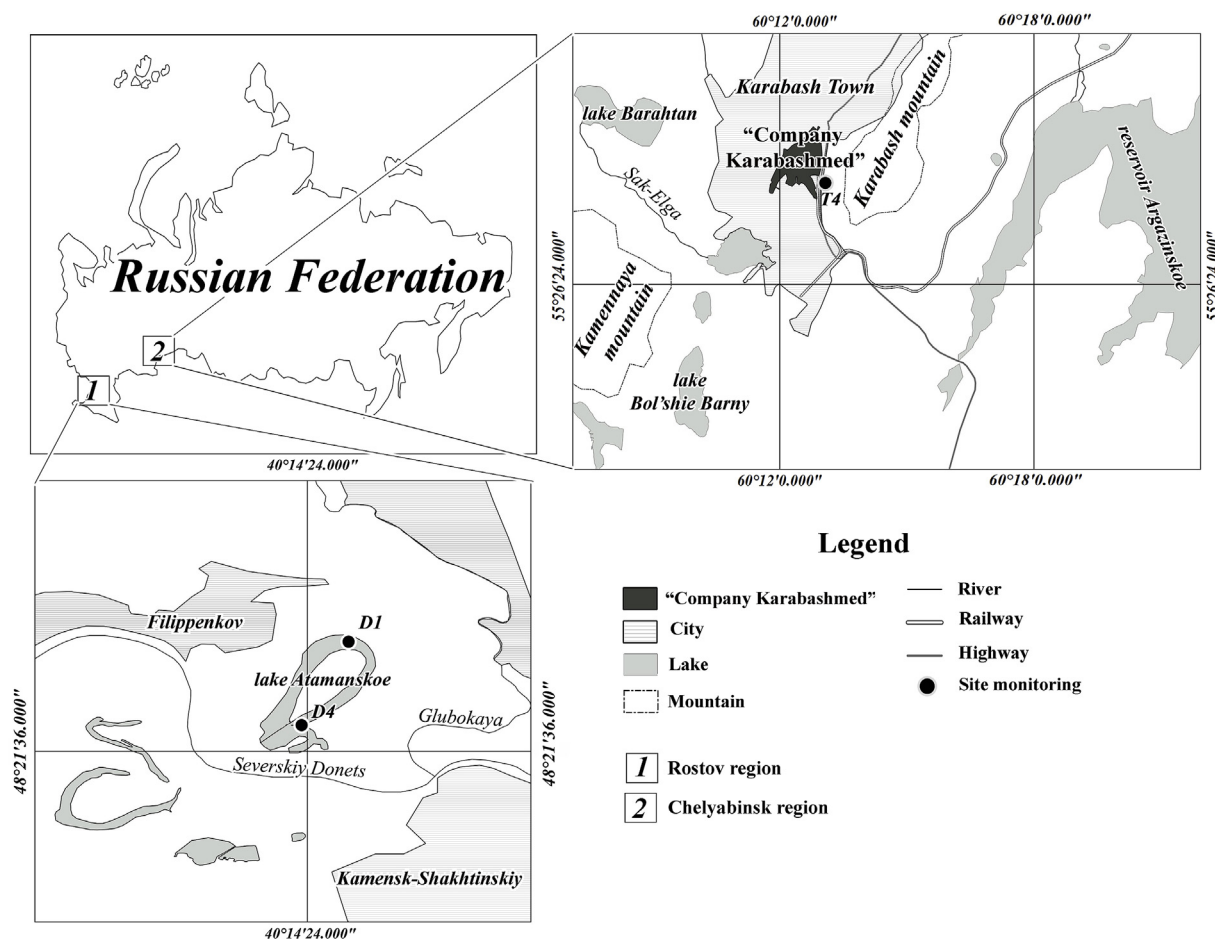
Fig. 1. General arrangement of the objects studied: industrial zone of Kamensk-Shakhtinskii (Rostov oblast, Southern Russia) and the region of the Karabash copper smelter (city of Karabash, Chelyabinsk oblast, Southern Urals). Monitoring plots are denoted by points.

horizons developing after 20 years in iron blast furnace wastes (Huot et al., 2013), formation of secondary clay minerals over 40 years in sulphidic mine spoils (Uzarowicz and Skiba, 2011), and development of a gossan layer in the upper 30 cm of sulphide tailings over 50 years weathering (Hayes et al., 2014).

Investigations in the geochemistry of technogenic landscapes should be based on the study of the molecular-structural state of objects rather than chemical elements. The determination of the fixation form and the type of the newly formed metal compound determine the volume, strength, and stability of metal fixation in highly dynamic physically and chemically heterogeneous ecological systems like the soil.

Selective chemical extraction methods are generally used for both understanding the chemistry of heavy metals (HMs) in their interaction with other soil properties (e.g. clay minerals, organic matter and the soil solution) and assessing their mobility and retention as well as their availability to plants (Cao et al., 2018; Heltai et al., 2018; Leopold et al., 2018). There are some problems when determining the availability and association of heavy metals with different geochemical soil fractions. The diverse chemicals used in the steps of chemical sequential extractions may alter the soil components in a different way, creating artefacts that depend on various factors, such as the choice and order of the releasing solutions, the length of the process, the solid/liquid ratio, and the procedure of sample preparation and conservation (Arenas-Lago et al., 2016; Filgueiras et al., 2002).

Methods for the direct determination of forms of HMs and metalloids in soils have developed actively in the last years. In the last 20 years, the methods of X-ray spectral diagnostics – X-ray absorption near-edge structure (XANES) and extended X-ray absorption edge fine

structure (EXAFS) – identified forms of many metals and metalloids in contaminated soils and sediments on the molecular level (Jacquat et al., 2009; Kirpichtchikova et al., 2006; Manceau et al., 2002; Minkina et al., 2014, 2016, 2017; Nevidomskaya et al., 2014, 2016). In particular, synchrotron X-ray micro-beam techniques can image the distribution of metal elements and solve the metal-bearing phases at the micrometer level (Terzano et al., 2007). Synchrotron-based micro-X-ray fluorescence (μ-XRF), and XAFS spectroscopy have been extensively utilized in soil systems to perform chemical speciation of Cu and Zn. μ-XRF, coupled with μ-XANES spectroscopy, has been used to investigate the distribution and speciation of soil Cu at the microscale (Strawn and Baker, 2009). Numerous studies have applied XAFS spectroscopy to determine Pb speciation in a variety of environments, including aerosol particles, soils, and street dusts (Barrett et al., 2010; MacLean et al., 2011; Terzano et al., 2007). Environmental magnetic methods have been widely used to investigate the degree, source, spatial distribution, and temporal evolution of anthropogenic pollution related to industrial and other human activities (Blundell et al., 2009; Bućko et al., 2011). The leading role of metal-bearing phases depending on the emission source and the type of chemical contamination was shown (Juillot et al., 2003; Manceau et al., 2002; Scheinost et al., 2002; Yu and Lu, 2016). It was revealed that the fixation of HMs by bearing phases depends on the soil composition and properties such as acid-base conditions (pH) and the amounts of organic matter, clay, carbonates, and Fe oxyhydroxides (Graf et al., 2007; Sipos et al., 2008; Strawn and Baker, 2009; Fernandez-Calvino et al., 2009).

In this context, it is important to have an idea of metal transformation (speciation) during the technogenic pedogenesis depending on

soil-forming conditions, soil properties, and contamination type.

The aim of this work was to study the speciation of metals (with Zn as an example) in contaminated technogenically transformed soils (Technosols in zones of anthropogenic anomalies in Southern Urals and Southern Russia) using a set of synchrotron X-ray methods.

2. Materials and methods

2.1. Site description and sampling

The objects of study were technogenic soils subjected to long-term anthropogenic load. The first object was territory of sludge collectors region of the Atamanskoe Lake natural basin, the city of Kamensk-Shakhtinskii, Rostov oblast, Southern Russia (Fig. 1). Lake Atamanskoe was used as a reservoir for the industrial wastes released from the chemical plant from the early 1960s to the mid-1990s. The lake contains 180 000 tons of flowing silts, 343 000 tons of low-plastic silts, and more than 444 000 tons of high-plastic silts (Privalenko et al., 2000). All these sediments are contaminated with HMs and organometallic compounds. According to the World Reference Base of Soil Resources (IUSS Working Group WRB, 2015), all the soil samples from plots D1 and D4 were classified as Spolic Technosols. The background soil is Fluvisol, typical for the studied area (IUSS Working Group WRB, 2015).

The other object included technogenic soils in the region of Karabash smelter (city of Karabash, Chelyabinsk oblast, Southern Urals), the largest and oldest copper-smelting complex in the Southern Urals (Fig. 1). Suburbs of the city of Karabash belong to the South-Ural mountainous landscape province with the dominance of Greyic Phaeozems Albic (IUSS Working Group WRB, 2015). Copper-smelting industry radically altered the landscape and the soils in the area. Technogenic pollution maximally affected the soils on Mount Zolotaya to the east of the Karabash copper smelter (Linnik et al., 2013). The Karabash sulfide tailings have a high concentrations of HMs, sulfide- and sulfate-S content. The average composition of wastes from Karabash smelter is as follows: sulfide – 6.3 wt %, $S_{sulfate}$ – 5.6 wt %, Fe – 7.7 wt %, Cu – 370 mg/kg, Zn – 330 mg/kg, Pb – 230 mg/kg, Sb – 33 mg/kg, and As – 170 mg/kg (Yurkevich et al., 2012). Natural ecosystems were destroyed because of long-term contamination of these areas. Plot T4 is located on the lower slope of Mount Zolotaya at only 0.75 km from the smelter and soil sample is classified as Spolic Technosol (IUSS Working Group WRB, 2015). The mount slope is covered by stony eluvial-deluvial deposits. The soil is similar to takyr; its thin loamy crust up to 1 cm thick breaks into polygonal blocks under drying. The western slope of Mount Zolotaya is bare.

Ecological situation is aggravated because of the absence of remediation works on these technogenic areas. Zinc is one of the most priority HMs containing in waste from chemical plants (Privalenko et al., 2000; Gashkina et al., 2015; Minkina et al., 2018).

To study the properties, contents, and transformation of Zn in soils, lithological survey of the area was performed, and plots adjacent to industrial zone of Kamensk-Shakhtinskii (Lake Atamanckoe region) and Karabash smelter were established (Fig. 1). At present, even if synchrotron sources are used, spectra of good quality in terms of the signal-to-noise ratio cannot always be detected for samples with low concentrations of absorbing metal (mg/kg). Therefore, to accomplish the purpose of this study, measurements were performed on the most contaminated monitoring plots of the objects under study.

2.2. Analytical methods

Soil sampling for physicochemical analyses and the subsequent cameral processing were performed according to ISO 10381-1 (2002). The soil particle size distribution was determined by the pipette method (with pyrophosphate procedure of soil preparation), ISO 13317-2 (2001). The methods used were for the determination of pH_{water} using a glass electrode in a 1:5 (volume fraction) suspension of soil in water,

ISO 10390 (2005); organic matter content by sulfochromic oxidation, ISO 14235 (1998); for carbonates content by using a Scheibler apparatus, ISO 10693 (1995); and determination of exchangeable cations using a hexamminecobalt trichloride solution, ISO 23470 (2011). A mineralogical analysis was performed by immersion microscopy method according to Methodological Recommendations (2008), which are in line with Russian standards. The total HMs content and the bulk chemical composition in the soils was determined by X-ray fluorescent (XRF) scanning spectrometer SPECTROSCAN MAKC-GV. The degree of soil contamination with HMs was estimated by comparing with the lithosphere clarkes (Vinogradov, 1957).

2.3. X-ray absorption spectroscopy

EXAFS, XANES, and XRD experimental data were obtained at the Structural Material Science Station at the 1.3b beamline of the Kurchatov Center of Synchrotron Radiation, Kurchatov Institute. A bending magnet with a field of 1.7 T of the Sibir'-2 storage ring was used as a source of synchrotron radiation at the 1.3 b beamline. During the generation of synchrotron radiation, the energy of electron beam was 2.5 GeV; mean current was 60–70 mA (Chernyshov et al., 2009).

Routine processing of experimental EXAFS spectra was performed using Fourier filtration and fitting the variable parameters of the local atomic structure model with the FEFFIT (Smolentsev and Soldatov, 2006) and Viper software. All spectra were normalized, and the oscillating part of the EXAFS function $\chi(k)$ was isolated from the absorption spectra. The threshold ionization energy E_0 was selected from the maximum of the absorption edge first derivative. Fourier transformation of the EXAFS function $\chi(k)$ was performed in the range of wave vectors k from $2.5\,\text{Å}^{-1}$ to $9.5\,\text{Å}^{-1}$ with the weight function k^2. Nonlinear fitting to experimental spectra was performed in the radius range of 0.12–0.25 nm.

2.4. X-ray diffraction method

Studies by the synchronous monochromatic X-ray diffraction method ($\lambda = 0.68,886\,\text{Å}$, Si monochromator) were conducted in transmission geometry using a Fujifilm imaging plate 2D detector at a wavelength of 0.68,886 Å. X-ray patterns were recorded in integrated mode at 20 °C. The exposure time of a sample was about 15 min. Powdered polycrystalline silicon (NIST SRM 640C) was used for the angular scale calibration. Experimental and calculated models of X-ray patterns for standard zinc-containing compounds from the Inorganic Crystal Structure Database (ICSD) were used.

2.5. Statistical analysis

All laboratory tests were performed in triplicate. The experimental data (means and standard deviations) were statistically processed using statistical functions of STATISTICA 10.0 software. Results were considered statistically significant at $p \leq 0.05$.

3. Results and discussion

3.1. Chemical and mineralogical composition

The combination of the chemical properties of Technosols (contents of clay and organic matter, pH) determines the buffer properties of the polydispersed system of Technosols. In uncontaminated Fluvisol, the content of C_{org} is 3.4 ± 0.1% at pH 7.3 ± 0.2 with insignificant amounts of carbonates found. The content of organic matter in Technosols around industrial zone of Kamensk-Shakhtinskii varied from 2.8 ± 0.1 to 4.4 ± 0.2, the pH values were from 7.3 ± 0.1 to 7.7 ± 0.2, and the reaction was estimated as slightly and medium alkaline (Table 1). Chemical compositions of the background uncontaminated soils and Technosoils are given in Table 1. The total Zn

Table 1

Physical and chemical properties of Technosols around industrial zone of Kamensk-Shakhtinskii (Southern Russia) and region of Karabash copper smelter (Southern Urals), and background soils ($n = 3$).

Sample/Parameter		Background soil	Around industrial zone of Kamensk-Shakhtinskii		Background soil	Region of Karabash copper smelter
			D1	D4		T4
C_{org},%		3.4 ± 0.1	2.8 ± 0.1	4.4 ± 0.2	4.5 ± 0.2	0.6 ± 0.04
pH_{water}		7.3 ± 0.2	7.3 ± 0.1	7.7 ± 0.2	6.7 ± 0.3	4.4 ± 0.1
$CaCO_3$, %		1.3 ± 0.02	7.8 ± 0.2	5.3 ± 0.3	n/d[a]	1.3 ± 0.1
Exchangeable Ca^{2+}, cmol (+)/kg		31.0 ± 2.4	29.2 ± 2.0	35.2 ± 1.7	11.1 ± 1.7	1.3 ± 0.1
Exchangeable Mg^{2+}, cmol (+)/kg		4.5 ± 0.3	4.8 ± 0.1	5.0 ± 0.2	3.1 ± 0.2	0.4 ± 0.02
Particle size fractions	sand (1.0–0.05 mm), %	13.8 ± 0.9	34.3 ± 2.0	28.3 ± 1.6	66.1 ± 3.7	75.4 ± 6.0
	silt (0.01–0.001 mm), %	53.8 ± 4.2	46.9 ± 2.8	38.7 ± 2.3	23.0 ± 1.2	24.5 ± 1.3
	clay (< 0.001, mm), %	32.4 ± 2.1	18.8 ± 1.6	33.0 ± 2.6	10.9 ± 0.7	0.1 ± 0.01
	SiO_2	62.8 ± 7.1	61.1 ± 4.1	54.8 ± 5.4	80.4 ± 6.2	50.4 ± 3.2
	Al_2O_3	14.7 ± 0.6	15.0 ± 0.8	11.8 ± 0.7	8.8 ± 0.6	15.7 ± 0.6
Chemical composition, wt %	Fe_2O_3	7.5 ± 0.3	7.9 ± 0.1	6.0 ± 0.1	3.7 ± 0.2	23.5 ± 1.6
	CaO	3.2 ± 0.1	3.6 ± 0.05	11.7 ± 1.0	1.2 ± 0.1	2.9 ± 0.1
	MgO	1.5 ± 0.09	1.3 ± 0.03	2.0 ± 0.1	1.1 ± 0.1	3.6 ± 0.2
	K_2O	2.1 ± 0.08	1.9 ± 0.03	1.4 ± 0.2	2.7 ± 0.2	1.8 ± 0.1
	P_2O_5	0.2 ± 0.02	0.2 ± 0.003	0.2 ± 0.01	0.3 ± 0.01	0.5 ± 0.02
	SO_3	0.03 ± 0.003	4.3 ± 0.03	7.3 ± 0.1	1.3 ± 0.1	1.1 ± 0.1
	Na_2O	1.0 ± 0.04	0.9 ± 0.02	0.9 ± 0.03	0.2 ± 0.01	0.9 ± 0.1

[a] (n/d) not detected.

Table 2

Total heavy metals and metalloids content of Technosols around industrial zone of Kamensk-Shakhtinskii (Southern Russia) and region of Karabash copper smelter (Southern Urals), and background soils ($n = 3$), mg/kg.

Sample/Metals and metalloids	Background soil[c]	Around industrial zone of Kamensk-Shakhtinskii		Background soil[d]	Region of Karabash copper smelter
		D1	D4		T4
As (1.7)[a]	1.2 ± 0.1	**12.9 ± 0.7**	**10.3 ± 0.5**	2.6 ± 0.1	**235.8 ± 13.6**
Cr (83)	97.9 ± 7.3	**152.8 ± 12.3[b]**	**154.1 ± 12.5**	100.0 ± 6.5	**436.8 ± 25.9**
Cd (0.13)	0.2 ± 0.003	**4.6 ± 3.5**	**10.6 ± 0.7**	0.20 ± 0.001	**4.8 ± 0.3**
Cu (47)	43.7 ± 3.2	**105.3 ± 9.0**	**146.9 ± 10.4**	18.0 ± 1.2	**1066.9 ± 70.7**
Mn (1000)	230.4 ± 66.9	615.6 ± 54.0	426.1 ± 51.0	1500 ± 82.8	**3374.8 ± 242.3**
Ni (58)	40.9 ± 2.6	81.7 ± 5.7	80.5 ± 6.4	35.0 ± 1.9	**991.5 ± 58.0**
Pb (16)	26.1 ± 1.7	**792.8 ± 69.5**	**1591.2 ± 129.3**	16.0 ± 1.1	**1233.6 ± 71.5**
Zn (83)	90.0 ± 7.6	**25,973.7 ± 1780.5**	**62,032.1 ± 5903.0**	60.0 ± 4.3	**10,953.2 ± 496.1**

[a] Lithosphere clark (Vingradov, 1957).
[b] Excesses over clark are highlighted in bold.
[c] According to Minkina et al. (2018).
[d] According to Chernien'kova (2002).

contents exceeding the lithosphere clark in hundreds of times were revealed in all examined samples because of technogenic soil formation (Table 2). Results of quantitative analysis (microscopic method) of the Technosols mineral phase revealed that autigenic minerals (sulfates, pyrite, carbonates) are predominant, which is due to the composition of pollutants contaminating the adjacent landscape for a long time (Table 3). Background soil of the Karabash area is Greyic Phaeozems Albic, which is characterized by the sub-neutral or weakly acid reaction of the soil profile with pH 6.7 ± 0.3, low content of organic matter, low sum of exchange cations, and the absence of carbonates (Table 1). Technosols from the region of Karabash copper smelter have acid reaction (pH 4.4 ± 0.1), low contents of organic matter (C_{org} 0.6 ± 0.04%), and low contents of fine fractions (Table 1). Magnetite, hematite, and magnetic spherules dominate the mineralogy and compose 50.0% of the total (Table 3).

3.2. Identification of Zn species at the XANES and EXAFS spectroscopy

Qualitative X-ray phase analysis was performed by comparing the experimental X-ray patterns with the model mineral phases from the ICSD database; it was shown that quartz is the dominating mineral phase in technogenic soils of all monitoring plots (Fig. 2). In the sample from monitoring plot T4, peaks of autigenic calcites, pyrite, and zinc

carbonate were revealed along with quartz. In monitoring plot D1, quartz was predominant; in soil of monitoring plot D4, a significant amount of calcite was revealed along with quartz. The diffraction patterns of both samples also contained diffraction peaks, which corresponded crystalline components composing the group of phyllosilicates: hydromuscovite (illite), kaolinite, gibbsite, and smectites as the mineral phase of montmorillonite (Fig. 2).

The sensitivity of the pre-edge region of XANES absorption spectra to the geometry of bonds can be used for the qualitative estimation of the molecular-structural state of the local Zn surrounding in soil samples from the objects studied. Zn XANES K edges in several standard compounds with the known structure (Zn–S (ZnS) and Zn–O (ZnO and $ZnSO_4$) bounds) show a significant difference in the position of absorption edge, which allows distinguishing these types of Zn surrounding in soil samples. Zn XANES K-edge spectra (Fig. 3) show a similarity of soil from monitoring plot D1 with the spectra of standards, in which Zn is coordinated by oxygen (ZnO, $ZnSO_4$), and the main absorption peak is at ~9670 eV. The XANES spectrum of soil sample D4 is similar to that of Zn, and its main absorption peak is at ~9665 eV. This agrees with the mineralogical analysis data, which revealed the dominant portion of autigenic sulfates (Table 3) formed during the long-term (up to 57 years) technogenic contamination (Privalenko et al., 2000). In the soil sample from monitoring plot D4, higher-energy

Table 3
Mineralogy of Technosols around industrial zone of Kamensk-Shakhtinskii (Southern Russia) and region of Karabash copper smelter (Southern Urals), and background soils (n = 3), %.

Sample	Terrigenic minerals													Autigenic minerals			
	Stable					Intermediate				Unstable				Iron hydroxides	Pyrite, marcasite	Carbonates	Sulfates
	Rutile	Zircon	Ilmenite	Kyanite	Sturolite	Apatite	Garnet	Epidote, zoisite	Varicolored mica	Amphibole	Muscovite, biotite	Magnetite, hematite	Pyroxene				
Background soil	4.0	8.0	5.0	tr[a]	4.0	n/d	n/d	n/d	n/d[b]	n/d	n/d	57.0	3.0	13.0	1.0	tr	5.0
D1	tr	8.0	8.0	tr	n/d	n/d	n/d	n/d	n/d	3.0	2.0	2.0	0.5	13.0	8.0	9.0	54.5
D4	tr	tr	12.0	tr	n/d	n/d	4.0	n/d	n/d	n/d	n/d	tr	n/d	20.0	8.0	tr	60.0
Background soil	2.0	1.0	5.0	tr	2.0	5.0	4.0	10.0	10.0	5.0	5.3	20.3	7.0	20.0	tr	n/d	tr
T4	0.1	0.1	3.4	0.3	0.5	0.1	1.0	11.5	2.4	12.5	1.0	50.0	12.0	3.6	1.1	tr	0.4

[a] (tr) trace.
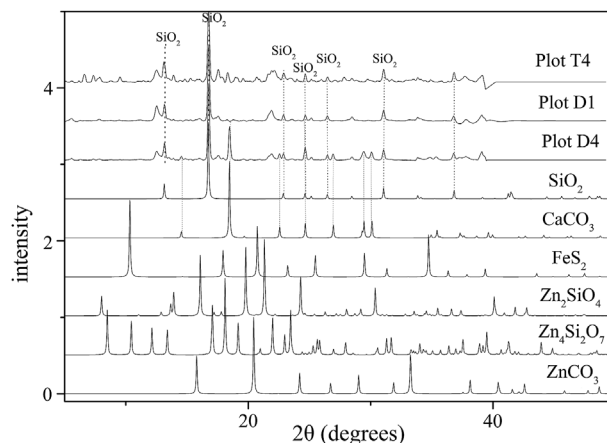[b] (n/d) not detected.

Fig. 2. X-ray powder diffraction patterns of experimental Technosols samples of the plot T4 (Karabash smelter region) and plots D1 and D4 (industrial zone of Kamensk-Shakhtinskii) compared to compounds selected from the ICSD database.
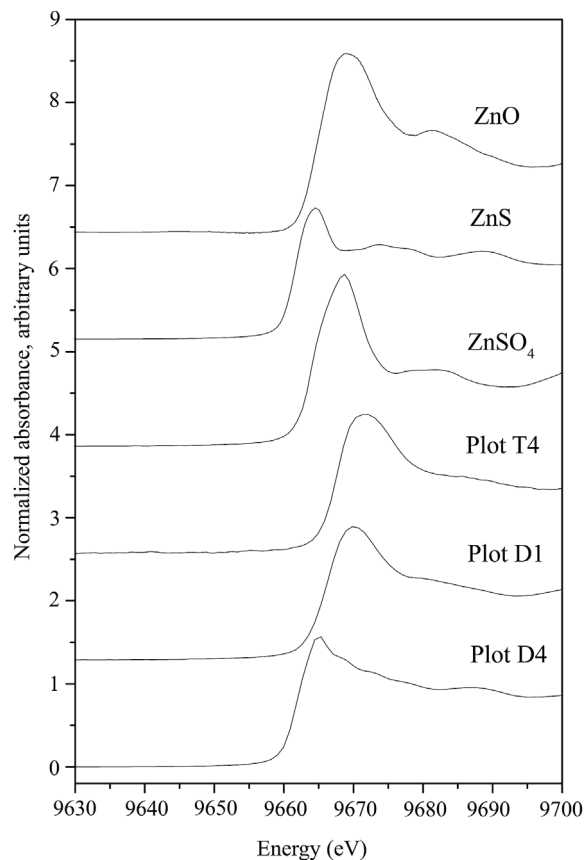

Fig. 3. Experimental K-edge XANES spectra of Technosols samples of the plot T4 (Karabash smelter region) and plots D1 and D4 (industrial zone of Kamensk-Shakhtinskii) compared to zinc-containing compounds.

features are also identified, which suggests the existence of mixed Zn–S and Zn–O bonds in the sample. In the region of the Karabash smelter, experimental spectra T4 were also measured and compared with the model spectra. It can be seen (Fig. 3) that the position and shape of the main features in the experimental spectrum are analogous to those observed in the spectrum of $ZnSO_4$, where the Zn atoms are coordinated by six oxygen atoms forming a deformed octahedron. Low symmetrical surrounding is formed because of the disturbance of bond lengths and angles and especially their appearance on the sites of local defects of the
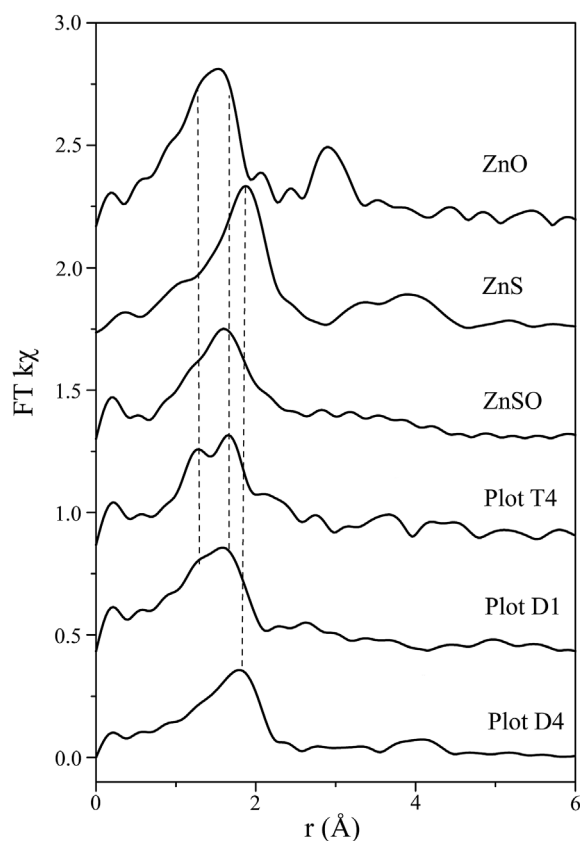
Fig. 4. Fourier transformants of EXAFS spectra χ(k) with weight coefficient k_2 of Technosols samples of the plot T4 (Karabash smelter region) and plots D1 and D4 (industrial zone of Kamensk-Shakhtinskii) compared to zinc-containing compounds.

crystalline lattice. The predominantly octahedral coordination of the Zn ion indicates the formation of hydrated adsorbed Zn and, probably, the existence of layered zinc phases (Vodyanitskii, 2010).

It was found (Juillot et al., 2003; Manceau et al., 2002; Schleget et al., 2001) that neoformation of technogenic phases, mainly Zn-containing phyllosilicates (clay minerals), occurs in highly contaminated soils. Layered Zn phases were revealed in the fraction bound to aluminosilicates (residual fraction) (Manceau et al., 2003; Scheinost et al., 2002); mechanism of Zn entry into the octahedral structures of layered minerals was established. These regularities obtained using XANES and EXAFS techniques agree with the results of the extractive fractionation of Zn in the studied soils (Minkina et al., 2016). This aligns with the mineralogical analysis of soil from plot T4, which revealed the dominant portion of autigenic magnetite and hematite constituting in total 50%, which confirms their technogenic origin due to long-term technogenic contamination (Gashkina et al., 2015).

Zn K-EXAFS spectra in *k* and *R* spaces for soil samples in comparison with the standard spectra of minerals ZnSO₄, sphalerite (ZnS), and zincite (ZnO) are shown in Fig. 4. In zincite, Zn atoms are tetrahedrally coordinated by oxygen atoms (first coordination sphere) with a mean wavelength of 1.98 Å; in addition, Zn atoms are surrounded by 12 neighboring Zn atoms at 3.23 Å on the average (Albertsson et al., 1989). Thus, two peaks observed on the radial distribution function for zincite at 1.5 Å and 2.9 Å (Fig. 4) correspond to the Zn–O and Zn–Zn distances, respectively. In the compound ZnSO₄, Zn is coordinated by four oxygen 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, as well as that of ZnO, contains a Zn–O peak, but the second Zn–Zn peak is almost absent because of the low coordination number. The Zn–S bond is 2.34 Å in ZnS, which is longer than the Zn–O bond in

ZnO and ZnSO₄ by 0.2–0.3 Å; therefore, the peak corresponding to Zn–S is observed at a longer distance in FT XAFS (Fig. 4). This obvious difference indicates different molecular-structural bonds Zn–S and Zn–O in soil samples D1 and D4.

The sufficiently high content of organic matter (Table 1) in Technosols around industrial zone of Kamensk-Shakhtinskii favors the interaction of ions Zn²⁺ with humic acids from the soil, which coordinate with functional groups and ligands and form tetrahedral Zn coordinations (Voegelin et al., 2005). The fine particle size largely affects the surface properties of mineral components, the adsorption capacity of the solid phase, and its buffer properties due to the forming mineral-organic Zn compounds (Fedotov et al., 2007; Petruzzelli et al., 1997).

Fourier transformants of the EXAFS spectrum for soil sample T4 from the Karabash copper smelter region (Fig. 4) also is more similar to the spectrum of ZnSO₄, than to other standards. However, it contains an additional intensive peak at low *R*, which is absent in all standard compounds and indicates the presence of short bonds forming by Zn atoms. The spectrum has no peaks corresponding to the second coordination sphere (Zn–Zn), which is observed on the radial distribution function of ZnO by 2.9 Å. This indicates a low content of ZnO in the sample. Other signs of the presence of Zn–S bonds in the sample are not found.

Analogously to XANES, K-edge Fourier transformants for Zn in two samples of Technosols from industrial zone of Kamensk-Shakhtinskii (lake Atamanskoe region) show obvious differences (Fig. 4), which confirm that Zn forms in these samples are different. The EXAFS Fourier transformant for soil sample D1 is highly similar to the analogous ZnSO₄ spectrum, although it contains an additional intensive peak at lower *R*. The absence of peak corresponding to the second coordination sphere (Zn–Zn) indicates that ZnO is not the dominant component of the sample. In soil from monitoring plot D4, the main peaks on the EXAFS Fourier transformant correspond to peaks of sphalerite, which points to the dominance of Zn–S bonds at the Zn atom. However, the additional peculiarity at lower *R* indicates the presence of Zn–O bonds. It is shown (Voegelin et al., 2005) that ZnO is transformed under soil contamination with zincite and predominantly enters into Zn-containing trioctahedral structures (up to 64% in the first year).

4. Conclusions

Speciation of Zn in Technosols was studied in regions of anthropogenic anomalies in Southern Urals and Southern Russia. It was found that the lithosphere clark for Zn is exceeded in hundreds of times in all of the studied soil samples.

Results of analysis by X-ray absorption spectroscopy revealed molecular-structural changes of Zn in highly contaminated natural-technogenic soils, which showed metal speciation under different natural conditions. This is of current importance for assessing the capacity of soil to protect the ecosystem against inorganic pollutants. A high degree of transformation was revealed in the composition of the mineral phase of Technosols, which is characterized by the dominant portion of autigenic minerals. The study of the molecular-structural organization of Technosols in Southern Urals established the type of the local surrounding of Zn, which is coordinated by six oxygen atoms forming a deformed octahedron. In the technogenically transformed soils of Southern Russia, the lengths of Zn–O bonds (which were close to those in ZnSO₄) and the mixed version of local surrounding with Zn–S and Zn–O bonds were determined.

Methods using synchrotron radiation are still less intensively used for soil studies, which is due to the complex organization of soil, its heterogeneity, and polydispersity. However, the expansion of their potentialities in the last years suggests that principally new knowledge about soils and mechanisms controlling the adsorption of different chemical substances by these soils would be acquired. These results should prove valuable in developing an effective remediation strategy.

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Appendix A. Supplementary data

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