



Geochemical transformation of soil cover and vegetation in a drained floodplain lake affected by long-term discharge of effluents from rayon industry plants, lower Don River Basin, Southern Russia

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Abstract Lake Atamanskoye is one of the most polluted aquatic environments in the South of Russia. This water body was affected by long-term pollution by effluent from industrial rayon plants located in the city of Kamensk-Shakhtinsky. Accumulation of pollutants resulted in the degradation of Lake Atamanskoye, which is currently drained. This research focused on the geochemical transformation of soils and vegetation within the territory of the former water body and its surroundings. Methods of study included the evaluation of potentially toxic elements (PTEs) in soils and plants by X-ray fluorescence, as well as the contents of their forms by sequential extraction and statistical processing of the data. The results revealed that *Spolic Technosols* and *Fluvisols* represent the most widespread soils within Lake Atamanskoye. The concentration of metals found in the soils of the lakebed is several orders of magnitude higher than the regional geochemical background and world soil baseline values due to long-term industrial pollution. The natural and technogenic soils were subdivided into two groups according to pH. Alkaline soils in the

presence of carbonates were characterised by high levels of PTEs, while acidic soils with higher proportions of exchangeable fractions and higher potential for metal accumulation in adjacent plants had lower levels of PTEs.

Keywords Floodplain · Potentially toxic element · Parallel sequential extraction · *Spolic Technosols* · Rayon industry · Bioaccumulation

Introduction

The textile industry, like most industrial sectors, is a source of chemical pollution (Hasanbeigi and Price 2015; Nimkar 2018; de Oliveira Neto et al. 2019; Shirvanimoghaddam et al. 2020). The textile industry includes an extensive group of industries engaged in the processing of natural and synthetic fibres into yarn and textiles. Textile production is a chemically intensive process and requires the use of potentially hazardous non-biodegradable chemicals, that contain sulphur, nitrates, acetic acid, soaps, naphthols, triphenyl methane, nitroso, azoic components, phthalocyanine, and formaldehyde-containing and hydrocarbon-based compounds, as well as PTEs, including chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb) (Rott and Minke 1999; Ramesh

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Babu et al. 2007; Wang 2010; Ghaly et al. 2014; Madhav et al. 2018; Nimkar 2018; Sivaram et al. 2019). These pollutants can enter the environment with solid wastes and wastewater. The most hazardous textile enterprises are those that produce semi-synthetic and synthetic fibres, in particular viscose rayon fibre, since the effluents from this process contain high concentrations of organic pollutants and metal ions (especially Zn^{2+}), in excess of the permissible values (Ghosh et al. 2011). The technological cycle of these plants involves using a concentrated solution of $ZnSO_4$ during viscose rayon regeneration. Subsequently, the contaminated solution is neutralised and discharged into a settling pond, where Zn precipitates and becomes a large component of the sludge (Moors and Dijkema 2006; Mamyachenkov et al. 2017). Many tons of Zn in the form $ZnSO_4$ is consumed annually in the production of rayon worldwide. Long-term accumulation of Zn-bearing effluents in dumps leads to the formation of significant volumes of sludge with the contents of Zn by dry weight varying from 6 to 23% or more (Mamyachenkov et al. 2017). Wastewater produced by such enterprises is usually stored in isolated artificially constructed basins that do not have direct contact with the environment. Potential processing of such sludge is a prospective method for recovery of zinc from industrial waste (Jha et al. 2007, 2008; Peng et al. 2008; Mamyachenkov et al. 2017).

One of the largest and oldest industrial centres for the production of synthetic fibres in Russia is located in Kamensk-Shakhtinsky, a city with a population of 89,000 people, located 130 km north of Rostov-on-Don. Textile and chemical enterprises in the city have used a number of natural water bodies in the floodplain of the Seversky Donets, including Soshnik, Rezak, Atamanskoye, and Polichka oxbow lakes, to discharge industrial effluent. Long-term wet dumping that occurred from the 1950s to the mid-1990s resulted in the degradation of these environments (Privalenko and Cherkashina 2012).

The Seversky Donets River is a tributary of the Don River, one of the largest rivers in the south of Russia. The presence of such a dangerous source of potential pollution in the Don River basin presents serious negative effects on the ecosystems of the entire Don Delta and the coastal parts of the Azov Sea (Minkina et al. 2016, 2017a, b; Tkachenko et al. 2017). Soils and vegetation in the floodplains play a vital role in the functioning of river basin systems (Tockner and

Stanford 2002). They are the most sensitive indicators of environmental health and hence pollution components in the ecosystems (Luster et al. 2014). In addition, the floodplains are dynamic and frequently subject to fluctuations in redox conditions and periodic flooding events (Overesch et al. 2007; Du Laing et al. 2009; Vodyanitskii and Savichev 2014; Skála et al. 2017; Davila et al. 2020). Accordingly, discharge into floodplain lakes of waste products containing high concentrations of hazardous substances pose great risks, and consequences to the environment and public health are difficult to predict (Aleksander-Kwaterczak and Helios-Rybicka 2009; Bogush and Lazareva 2011).

Previous studies of floodplain soils of the Seversky Donets River valley show that long-term accumulation of hazardous effluents has degraded the natural water bodies and formed technogenic soils with anomalous contents of PTEs and other contaminants that exceed permissible levels by orders of magnitude (Bauer et al. 2018; Sushkova et al., 2020). These studies reveal relationships between mineralogical composition and various forms of PTEs and characterise factors related to their mobility (Minkina et al. 2018a, 2019; Vodyanitskii and Minkina 2019; Vodyanitskii et al. 2020). This research focused on the spatial distribution of soil pollution with respect to Cr, Mn, Ni, Cu, Zn, Cd, and Pb in the soils of former Lake Atamanskoye and adjacent areas and identified peculiarities of the geochemical transformation of floodplain vegetation under extremely high pollution.

Materials and methods

Study area and sample collection

Lake Atamanskoye ($48^{\circ} 21' 00''$ N, $40^{\circ} 14' 30''$ E), located in the floodplain of the Seversky Donets, a large right-bank tributary of the Don River (Fig. 1), occupies the area of 0.36 km^2 . Soil-forming rocks in the research area are represented by modern alluvial deposits of different ages (Klimenko and Kryshchenko 1978). The climate of the region is classified as humid continental without a dry season and with hot summers; the average annual temperature is 8.9°C , and annual rainfall reaches 460 mm (Climate-Data.org 2020). Snowmelt waters are the main source of nutrition for the Seversky Donets. Spring flooding

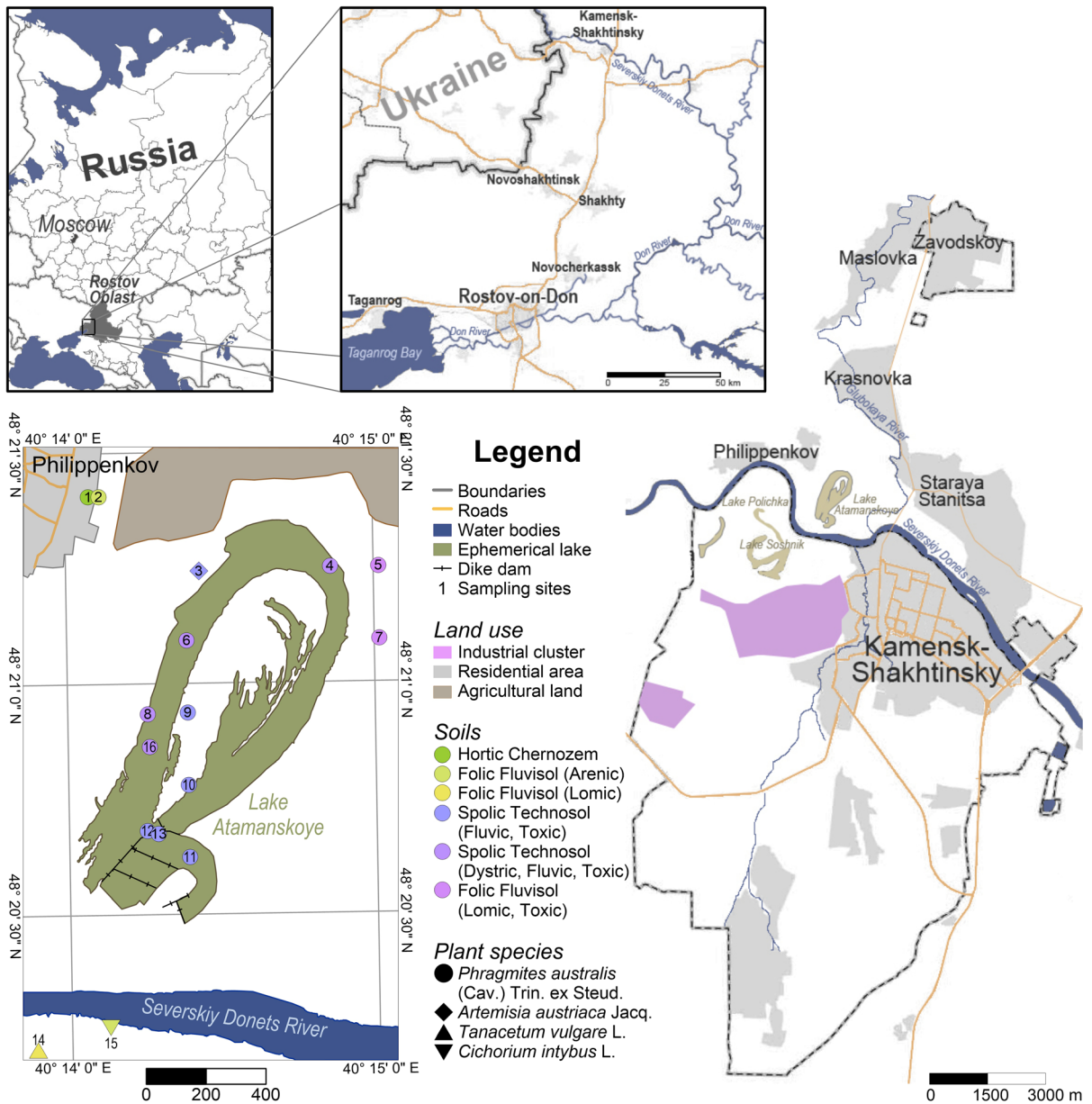


Fig. 1 Simplified map of Lake Atamanskoye and location of sampling sites

occurs from February through April and is accompanied by a rise in water level of 3–8 m. Lake Atamanskoye is characterised by a pulsating water regime similar to other floodplain water bodies in the region. The reservoir is an old oxbow with a ragged lakebed, which formed because of changes in the hydrological regime of the lake caused by the

discharge of toxic effluents into the water body of the reservoir. Since the mid-1990s, the lake has not been used for wet dumping and does not appear in the State register of waste disposal facilities. The results of hydrogeological studies conducted before the complete disappearance of the lake showed that bottom sediments were technologically transformed

into well-stratified sludge, equivalent to rich ores in terms of the metal concentrations. Total reserves of Zn in technogenic sediments of Lake Atamanskoye were estimated at 30 kt (Privalenko and Cherkashina 2012).

In this study, the soils and vegetation at 16 monitoring sites in the vicinity of Lake Atamanskoye were analysed (Fig. 1). The soils at the sites were classified according to the World Reference Base of Soil Resources (IUSS Working Group WRB 2015). *Folic Fluvisols* are formed on stratified fluvial sediments of various texture within the floodplain of the Seversky Donets. The soils in the lakebed of the former Lake Atamanskoye, in which sewage sludge from textile production was dumped over a long period of time, comprise *Spolic Technosols (Fluvisol, Toxic)*. *Folic Fluvisols (Lomic, Toxic)* appear in the peripheral parts of the former lake. High river terraces are *Chernozems* on loess-like loams under the steppe vegetation. Soil samples were collected from the surface soil horizon (0–20 cm deep) in June 2019 using the envelope method (GOST 17.4.4.02-2017 2018). The soil samples were air-dried, mixed, ground, and passed through a 1-mm sieve (Vorobyova 2006). The dominant plant species sampled were *Phragmites australis* (Cav.) Trin. Ex Steud., *Tanacetum vulgare* L., *Cichorium intybus* L., and *Artemisia austriaca* Jacq. (Fig. 1). The plant samples collected from each sampling site were mixed together and then separated into stems and roots for comparative laboratory analysis.

Analytical methods

The particle size analysis was conducted using the pipette method and a pyrophosphate procedure of soil preparation (Soil Survey Staff 2011) to obtain the clay fraction (particles < 0.002 mm). The total organic carbon (TOC) content in the soils was determined using the dichromate oxidation method according to Tyurin (Vorobyova 2006). The pH was measured by potentiometry in the supernatant suspension of soil and water in a ratio of 1:5 (ISO 10390:2005 2005). The CaCO₃ content was determined by the complexometric method proposed by Kudrin (Vorobyova 2006). The exchangeable cations Ca²⁺ and Mg²⁺ were determined using the method described by Shaimukhametov (1993).

The total concentrations of Cr, Mn, Ni, Cu, Zn, Cd, and Pb were determined by XRF analysis using a

Spectroscan MAX-GV spectrometer (Spectron, Russia, OST 10-259-2000 2001). Parallel sequential extraction of PTEs in the three chemical fractions was carried out using the combined scheme proposed by Minkina et al. (2018b). Loosely-bound compounds of PTEs were defined as follows: (1) exchangeable fraction (weakly bound acid-soluble), (2) complex fraction (organically-bound, complex compounds), and (3) specifically absorbed fraction (bound to amorphous compounds and carbonates). The exchangeable fraction was extracted using an ammonium acetate buffer solution with pH 4.8 (NH₄Ac) and a soil/solution ratio of 1:10 for 18 h. The concentrations of metals in complex compounds were determined as the difference between the concentrations in the NH₄Ac extract and the extract prepared with 1% EDTA (ethylenediaminetetraacetic acid) in NH₄Ac at a soil/solution ratio of 1:10 for 18 h. The specifically absorbed fraction was extracted with 1 mol/L HCl at a soil/solution ratio of 1:10 for 1 h. The extract from each step was filtered through a paper filter (2–3 μm) and determined by atomic absorption spectrophotometry (AAS, KVANT 2-AT, Kortec Ltd, Russia, RD 52.18.289-90 1990). Plants were prepared for analysis by dry combustion at 450 °C, and PTEs were dissolved by an acid mixture (HNO₃ + HCl). Concentrations of PTEs in plant extracts were determined by the AAS analyser.

All laboratory tests were performed in triplicate. The accuracy of element determination was verified using duplicates, reagent blanks, and state standard reference samples (no. GSS 10412-2014, State Service for Standard Specimens Relating to Composition and Properties of Substances and Materials), and complies with standards of certified methods (RD 52.18.289-90 1990 and OST 10-259-2000 2001).

Data analysis

The software package STATISTICA 12 (StatSoft, USA) was used for statistical analysis of the data. Basic descriptive statistics including mean, median, minimum, maximum, standard deviation (SD), and coefficient of variation (CV) were computed for both physical–chemical parameters and PTEs (Tables 1 and 2). Pearson correlation coefficients (*r*) and hierarchical cluster analysis (HCA) were applied to the analytical data to test the interaction between PTEs in soils and plants. HCA was performed according to

Table 1 Descriptive statistics of soil physical–chemical properties

| Soil | n | pH | Clay (< 0.002 mm) (%) | TOC (%) | CaCO ₃ (%) | Exchangeable cations (cmol(+)/kg) | |
|--|---|-----------------------------|---------------------------------------|-----------------------------|-----------------------------|--------------------------------------|-----------------------------|
| | | | | | | Ca ²⁺ | Mg ²⁺ |
| <i>Hortic Chernozem</i> | 1 | 7.3 | 32.4 | 2.0 | 1.3 | 31.0 | 4.5 |
| <i>Folic Fluvisol (Arenic)</i> | 2 | <u>7.7 ± 0.2</u> 7.5–7.8 | <u>5.9 ± 6.1</u> <u>1.6–10.2</u> | <u>1.3 ± 0.5</u> 0.9–1.6 | <u>0.5 ± 0.5</u> 0.1–0.8 | <u>8.9 ± 4.1</u> 6.0–11.8 | <u>1.1 ± 0.6</u> 0.6–1.5 |
| <i>Folic Fluvisol (Lomic)</i> | 1 | 7.4 | 28.4 | 2.2 | 0.1 | 26.5 | 3.3 |
| <i>Spolic Technosol (Fluvic, Toxic)</i> | 6 | <u>7.8 ± 0.2</u> 7.4–8.0 | <u>17.3 ± 5.0</u> <u>10.8–23.3</u> | <u>1.7 ± 0.5</u> 1.2–2.6 | <u>3.7 ± 1.8</u> 0.3–5.3 | <u>26.3 ± 6.6</u> 18.5–35.3 | <u>3.4 ± 1.2</u> 2.0–5.0 |
| <i>Spolic Technosol (Dystric, Fluvic, Toxic)</i> | 4 | <u>3.9 ± 0.4</u> 3.4–4.4 | <u>15.7 ± 7.2</u> <u>9.6–25.6</u> | <u>2.2 ± 1.0</u> 1.6–3.6 | 0.0 | <u>28.1 ± 7.0</u> 18.8–35.6 | <u>3.1 ± 0.8</u> 2.0–4.0 |
| <i>Folic Fluvisol (Lomic, Toxic)</i> | 2 | <u>6.0 ± 1.6</u> 4.8–7.1 | <u>14.4 ± 7.9</u> <u>8.8–20.0</u> | <u>1.9 ± 0.1</u> 1.8–1.9 | <u>1.0 ± 1.3</u> 0.0–1.9 | <u>30.3 ± 2.5</u> 28.5–32.1 | <u>3.2 ± 0.6</u> 2.7–3.6 |

The mean ± SD is above the line, min–max values are below the line, n is the number of soil samples, and TOC is the total organic carbon

Table 2 Descriptive statistics of PTE content (mg/kg) in soils (n = 16)

| Fraction | Mean | Median | Minimum | Maximum | SD | CV | RB | GB _{UCC} | GB _{ws} |
|-----------------------|----------|--------|---------|----------|----------|-------|-------|-------------------|------------------|
| Cr | | | | | | | | | |
| Total | 124.5 | 113.5 | 51.0 | 240.0 | 49.9 | 40.0 | 90.5 | 92.4 | 59.5 |
| Exchangeable | 5.6 | 5.4 | 0.7 | 11.6 | 3.6 | 64.0 | | | |
| Complex | 9.0 | 7.8 | 0.8 | 30.9 | 8.1 | 90.1 | | | |
| Specifically absorbed | 14.2 | 14.5 | 2.6 | 40.6 | 10.6 | 74.6 | | | |
| Mn | | | | | | | | | |
| Total | 830.5 | 682.0 | 223.0 | 2651.0 | 661.1 | 79.6 | 800.6 | 770 | 488 |
| Exchangeable | 50.3 | 55.8 | 5.0 | 112.9 | 32.3 | 64.3 | | | |
| Complex | 104.8 | 64.3 | 7.7 | 370.6 | 106.7 | 101.8 | | | |
| Specifically absorbed | 173.8 | 165.3 | 33.5 | 463.9 | 129.7 | 74.6 | | | |
| Ni | | | | | | | | | |
| Total | 86.6 | 68.0 | 19.0 | 266.0 | 64.6 | 74.6 | 42.5 | 50 | 29 |
| Exchangeable | 3.5 | 1.9 | 0.1 | 9.1 | 3.4 | 96.5 | | | |
| Complex | 10.5 | 6.9 | 1.8 | 41.1 | 10.9 | 103.8 | | | |
| Specifically absorbed | 18.3 | 12.5 | 1.9 | 87.2 | 20.9 | 114.1 | | | |
| Cu | | | | | | | | | |
| Total | 192.4 | 161.5 | 15.0 | 527.0 | 163.3 | 84.8 | 43.8 | 39 | 38.9 |
| Exchangeable | 17.2 | 10.1 | 0.1 | 46.8 | 17.2 | 100.3 | | | |
| Complex | 40.7 | 27.8 | 1.6 | 134.7 | 41.3 | 101.3 | | | |
| Specifically absorbed | 73.4 | 50.7 | 2.9 | 250.3 | 75.0 | 102.1 | | | |
| Zn | | | | | | | | | |
| Total | 23,839.3 | 4844.0 | 85.0 | 66,075.0 | 28,277.3 | 118.6 | 71.3 | 75 | 70 |
| Exchangeable | 4687.9 | 1507.0 | 7.1 | 13,498.0 | 5297.8 | 113.0 | | | |
| Complex | 4150.8 | 925.2 | 6.0 | 13,120.0 | 5193.6 | 125.1 | | | |
| Specifically absorbed | 10,213.3 | 1811.0 | 16.0 | 29,890.0 | 12,473.1 | 122.1 | | | |

Table 2 continued

| Fraction | Mean | Median | Minimum | Maximum | SD | CV | RB | GB _{UCC} | GB _{ws} |
|-----------------------|-------|--------|---------|---------|-------|-------|------|-------------------|------------------|
| Cd | | | | | | | | | |
| Total | 6.3 | 3.9 | 0.3 | 30.0 | 7.8 | 122.7 | 0.3 | 0.64 | 0.31 |
| Exchangeable | 1.2 | 0.1 | 0.0 | 10.1 | 2.6 | 216.3 | | | |
| Complex | 1.1 | 0.2 | 0.0 | 5.7 | 1.8 | 159.5 | | | |
| Specifically absorbed | 2.5 | 1.7 | 0.0 | 11.2 | 2.9 | 116.3 | | | |
| Pb | | | | | | | | | |
| Total | 544.9 | 175.5 | 20.0 | 2301.0 | 702.7 | 129.0 | 22.2 | 17 | 27 |
| Exchangeable | 66.8 | 18.6 | 0.9 | 487.4 | 124.1 | 185.7 | | | |
| Complex | 109.2 | 30.3 | 1.1 | 451.1 | 153.6 | 140.7 | | | |
| Specifically absorbed | 219.5 | 46.0 | 2.3 | 949.2 | 305.1 | 139.0 | | | |

SD standard deviation, CV coefficient of variation, RB regional geochemical background (Mandzhieva et al. 2017; Minkina et al. 2017b), GB_{UCC} upper continental crustal content of metal (Grigoriev 2009), GB_{ws} world soil average content of metal (Kabata-Pendias 2011)

Ward's method, and the measure of similarity was the 1-Pearson r , and the results are reported in the form of a dendrogram. The critical level of amalgamation for a set of 16 samples was 0.503 at $p < 0.05$. Data visualisation was conducted using Grapher 11 (Golden Software, USA), and maps were generated using Surfer 12 (Golden Software, USA).

Soil pollution indices and plant uptake calculations

Pollution levels of PTEs in the soils were evaluated using the geoaccumulation index (I_{geo}) introduced by Müller (1986), the pollution index (PI), and the Nemerow pollution index (NPI). The I_{geo} in comparison with PI reduces the influence of lithogenic variability in element content expressed in the following equation:

$$I_{\text{geo}} = \log_2 \left(\frac{C_i}{1.5\text{RB}} \right), \quad (1)$$

where C_i is the total content of metal i in a soil sample and RB is the regional background value (Table 2). The I_{geo} is ranked into seven classes (Müller 1986): unpolluted (≤ 0), unpolluted to moderately polluted (0–1), moderately polluted (1–2), moderately to highly polluted (2–3), highly polluted (3–4), highly to extremely polluted (4–5), and extremely polluted (> 5).

The PI is the simple ratio of the element content to the RB calculated as:

$$\text{PI} = \frac{C_i}{\text{RB}}, \quad (2)$$

The following soil contamination classes were identified according to PI values (Kowalska et al. 2018) as: absent (< 1), low (1–2), moderate (2–3), strong (3–5), and very strong (> 5) contamination.

The NPI was used to assess the soil pollution for the total of all elements studied, regardless of their quantity (Nemerow 1974), as shown below:

$$\text{NPI} = \sqrt{\frac{\left(\frac{1}{n} \sum_{i=1}^n \text{PI}_i\right)^2 + \text{PI}_{\text{max}}^2}{2}}, \quad (3)$$

where PI_i is the calculated value of the pollution index of the i -th metal, PI_{max} is the maximum value for all PTEs, and n is the number of PTEs. Five classes of the soil quality were defined by NPI (Kowalska et al. 2018): clean (≤ 0.7), warning limit (0.7–1.0), slight pollution (1–2), moderate pollution (2–3) and heavy pollution (≥ 3).

The PTE uptake from the soil into roots and shoots was calculated using Eqs. (4) and (5) according to Bech et al. (2014):

$$\text{BCF} = \frac{C_{\text{root}}}{C_{\text{soil}}} \quad \text{and} \quad (4)$$

$$\text{TF} = \frac{C_{\text{stem}}}{C_{\text{root}}}, \quad (5)$$

The bioconcentration factor (BCF) is the soil-to-plant element mobility index, which indicates the degree of biophilicity of elements (Chaplygin et al. 2018). Hyperaccumulators always have a BCF greater than 1 and sometimes even range from 50 to 100 (Lago-Vila et al. 2015), while a BCF of 1 indicates a rather indifferent behaviour of the plant towards metals, and a BCF < 1 shows that the plant excludes metals from uptake (Serbula et al. 2012). The translocation factor (TF) makes it possible to evaluate plant protection mechanisms, which, as a rule, prevents the metal translocation to above-ground phytomass (Antoniadis et al. 2017; Enya et al. 2019). Plants usually have a TF < 1 at metal stress, which also indicates the potential for phytostabilisation, and TF > 1 indicates hyper-accumulative plants that tolerate contamination and can be used for phytoextraction (Bech et al. 2014; Chaplygin et al. 2018).

Results and discussion

Physical–chemical properties of studied natural and technogenic soils

The natural and technogenic soils studied here present a striking contrast. Descriptive statistics for the main physical–chemical properties of the soils are presented in Table 1. It is clear that technogenic soils, occupying the lakebed, differ in terms of their properties. *Spolic Technosols* (*Dystric*, *Fluvic*, *Toxic*) are extremely acidic (pH 3.9 ± 0.4), while *Spolic Technosols* (*Fluvic*, *Toxic*) are slightly alkaline (pH 7.8 ± 0.2) and contain carbonates ($3.7 \pm 1.8\%$). Both acid and alkaline *Technosols* are classified as sandy loam and characterised by comparable contents of exchangeable cations and organic carbon. Variations in pH values and CaCO₃ contents in studied *Technosols* with a similar genesis can be explained as a result of wet dumping in a floodplain water body over a long period of time. Subsequent differences in soil properties may be associated with unstable chemical compositions of effluents, which depend on the technological processes and raw materials used at the industrial rayon plants. It is also important to mention that the sedimentation of technogenic material in a floodplain lake is affected by the topography of the lakebed, the

location of engineering structures such as dams and pipes, and the occurrence of large floods.

In fact, the time for pedogenesis, as well as the vegetation and water regimes, can differ significantly for such technogenic landscapes, which in turn leads to the variations in the intensity of biological processes and carbonate leaching (Santini and Fey 2016; Uzarowicz et al. 2017; Betancur-Corredor et al. 2020; Konstantinov et al. 2020). *Folic Fluvisols* (*Lomic*, *Toxic*) are moderate to slightly acidic (pH 6.0 ± 1.6) and contain a rather high content of clay fraction (Table 1) because this soil developed on limnic alluvial sediments and the upper horizons can be enriched with fine fractions of natural or technogenic origin during flooding events. The TOC content (1.9 ± 0.1) and the exchangeable cations are similar to those in *Spolic Technosols*, which indicates of the strong influence of wet dumping on these soils. *Folic Fluvisols* (*Arenic*)/(*Lomic*) represent typical variants of alluvial soils in the study area. They are slightly alkaline (pH 7.4–7.8), and characterised by low CaCO₃ content (< 1%) and lower TOC than that found in natural and technogenic soils of the floodplain lake. The loamy texture is characteristic of *Fluvisols* of Seversky Donets floodplain from a small sandy seasonal stream at the base of an erosional form. *Chernozems* represent the background soil in the study area, although in the vicinity of Lake Atamanskoye, they have been significantly transformed by human activity. *Hortic Chernozem* studied within the vicinity of Phillipenkov village was characterised by neutral reactions in the upper horizon (pH 7.3) and rather low TOC content (2.0%) for *Chernozems*, which is probably related to long-term anthropogenic transformation.

Content of PTEs in soils

Table 2 summarises the data on the contents of Cr, Mn, Ni, Cu, Zn, Cd, and Pb, as well as their fractions for both background soils and soils affected by wet dumping in Lake Atamanskoye. The total concentrations of individual elements studied varied significantly. High values of the CV (> 33%) were observed for all metals (from 40.0 for Cr to 122.7 for Cd), indicating high heterogeneity among samples, which is typical for the areas affected by extreme pollution. The metals, in descending order of average total concentrations, are: Zn > Mn > Pb > Cu > Cr >

Ni > Cd. The highest mean value was observed for Zn (23.8 g/kg), which is more than 300 times higher than global and regional background values (Table 2). The data confirm that Zn is the most abundant soil contaminant in the study area. On average, the total content of Cd and Pb in the soils of the former Lake Atamanskoye is an order of magnitude higher than the background soils, while the contents of the remaining metals are only slightly higher (Ni and Cu) or comparable (Cr and Mn) to background values. When these metals were compared with baseline concentrations of these elements in the upper continental crust (Grigoriev 2009) and world soil average values (Kabata-Pendias 2011), a similar pattern was observed.

Figure 2 presents box-plots of total PTEs in different soils from Lake Atamanskoye. The lowest concentrations were observed for background soils and the highest for *Technosols* developed within the lakebed of Lake Atamanskoye. It is possible to rank the different natural and technogenic soils within the studied area according to the content of metals; in descending order, they are: *Spolic Technosols (Fluvic, Toxic)* > *Spolic Technosols (Dystric, Fluvic, Toxic)* > *Folic Fluvisols (Lomic, Toxic)* > *Folic Fluvisol (Lomic)* > *Hortic Chernozems* > *Folic Fluvisol (Arenic)*. The highest total concentration of all metals was observed in alkaline *Technosols*, while concentrations in acidic *Technosols* were several times lower (most of the metals studied are not mobile in soils of high pH).

In terms of individual fractions of metals, the highest differences between minimum and maximum values were observed for exchangeable fractions, which were two or more orders of magnitudes higher in heavily polluted technogenic soils in comparison with background soils. For complex and specifically absorbed forms, the differences were 1–2 orders of magnitude higher. For Zn and Cd, all forms were higher by three or more orders of magnitude in comparison with unpolluted soils.

Partitioning of metals in natural and technogenic soils

Figure 3 represents a partitioning of Cr, Mn, Ni, Cu, Zn, Cd, and Pb forms in soils from different sampling sites from Lake Atamanskoye and its surroundings. For Cr, which is not directly related to pollution by effluents from the rayon industry, the highest

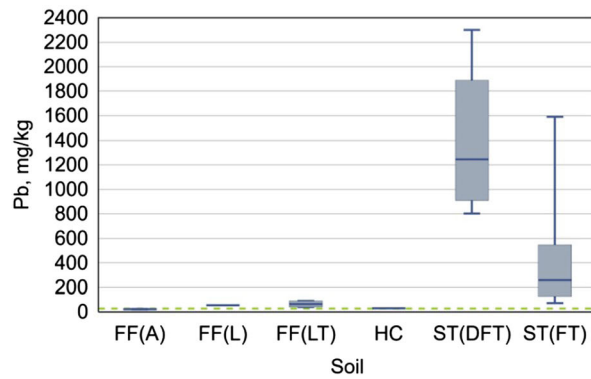
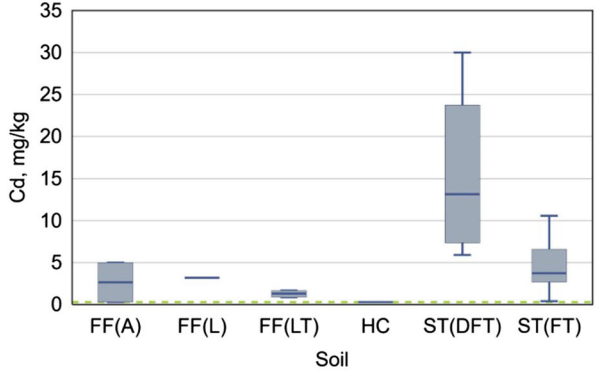
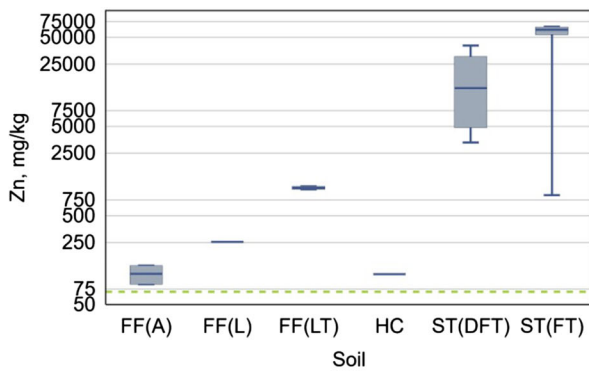
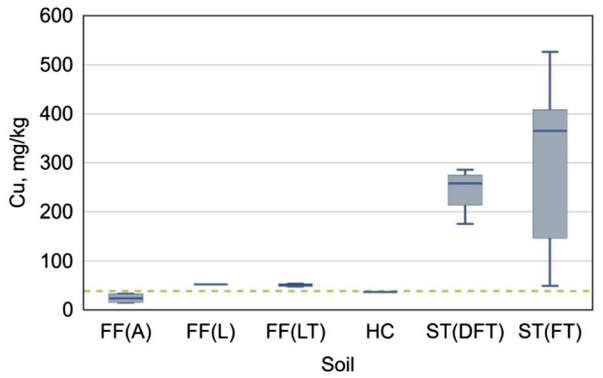
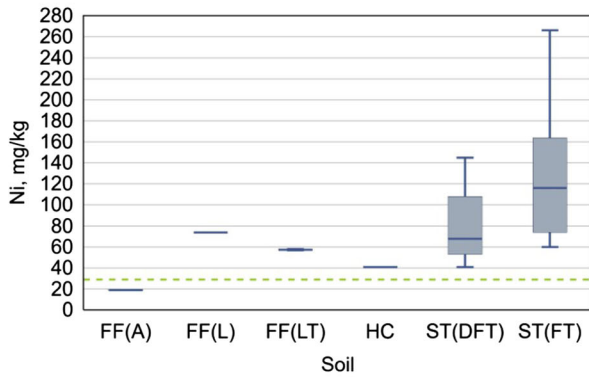
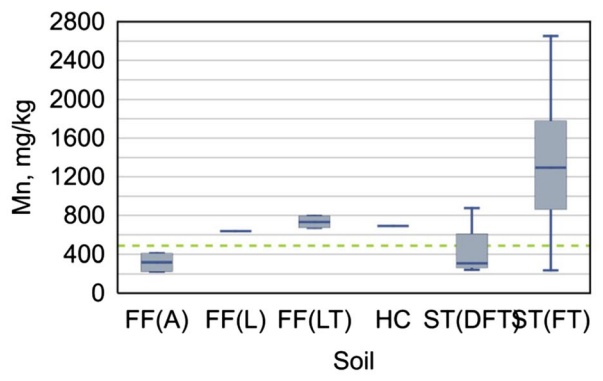
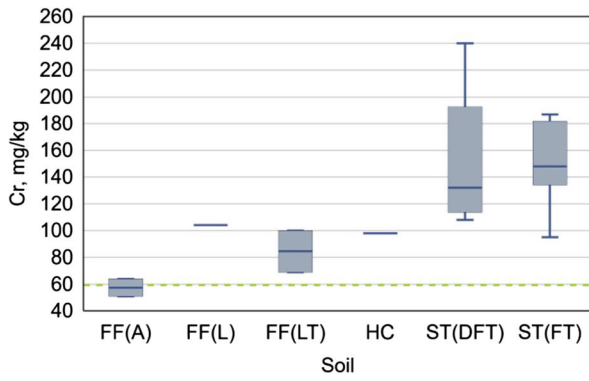
Fig. 2 Box-plots of total PTE content in different soils from Lake Atamanskoye: FF(A)—*Folic Fluvisol (Arenic)*, FF(L)—*Folic Fluvisol (Lomic)*, FF(LT)—*Folic Fluvisol (Lomic, Toxic)*, HC—*Hortic Chernozem*, ST(DFT)—*Spolic Technosol (Dystric, Fluvic, Toxic)*, ST(FT)—*Spolic Technosol (Fluvic, Toxic)*. The dashed line represents the average world soil content of PTEs

proportion was characteristic of its residual form, which comprised 70–95% of the all forms in the studied samples. In total, it was possible to rank the forms of Cr in descending order as: residual > specifically absorbed > complex > exchangeable. There was a similar tendency for Mn, although in heavily polluted soils with lower pH values (*Spolic Technosols (Dystric)* and *Folic Fluvisols (Lomic, Toxic)*), the proportions of specifically absorbed and complex forms increased significantly. For Ni, the raw metal forms were similar to those of Cr, although in alkaline *Spolic Technosols* in the presence of carbonates, the proportion of specifically absorbed and complex forms was rather high, reaching the values of 50% above the total.

For Zn, Cu, Cd, and Pb, which are the most typical pollutants related to rayon industry effluents, the proportion of forms in heavily contaminated soils was quite different from Cr, Mn, and Ni. In terms of Cu, Cd, and Pb, most of the samples showed the following relative proportions: specifically absorbed > residual > complex > exchangeable, except for *Spolic Technosols (Dystric)* with low pH values, for which the proportion of complex forms was higher than the residual forms. A different situation was observed for Zn, and in most of the contaminated soils, it was ranked from highest to lowest as: specifically absorbed > exchangeable > complex > residual. The high proportion of the most mobile forms of Zn, as well as anomalous concentrations of this element, predetermine high risks related to the potential migration of this metal in a dynamic environment with redox fluctuations.

Relationship between PTEs and soil physical–chemical properties

The results of Pearson correlations between total PTE content and soils properties are presented in Table 3. Medium and strong positive correlations ($p < 0.05$) were observed for the following pairs of metals: Cr–Ni (0.66), Cr–Cu (0.716), Cr–Zn (0.722), Mn–Ni (0.664), Mn–Cu (0.511), Mn–Zn (0.604), Ni–Cu (0.511), Ni–



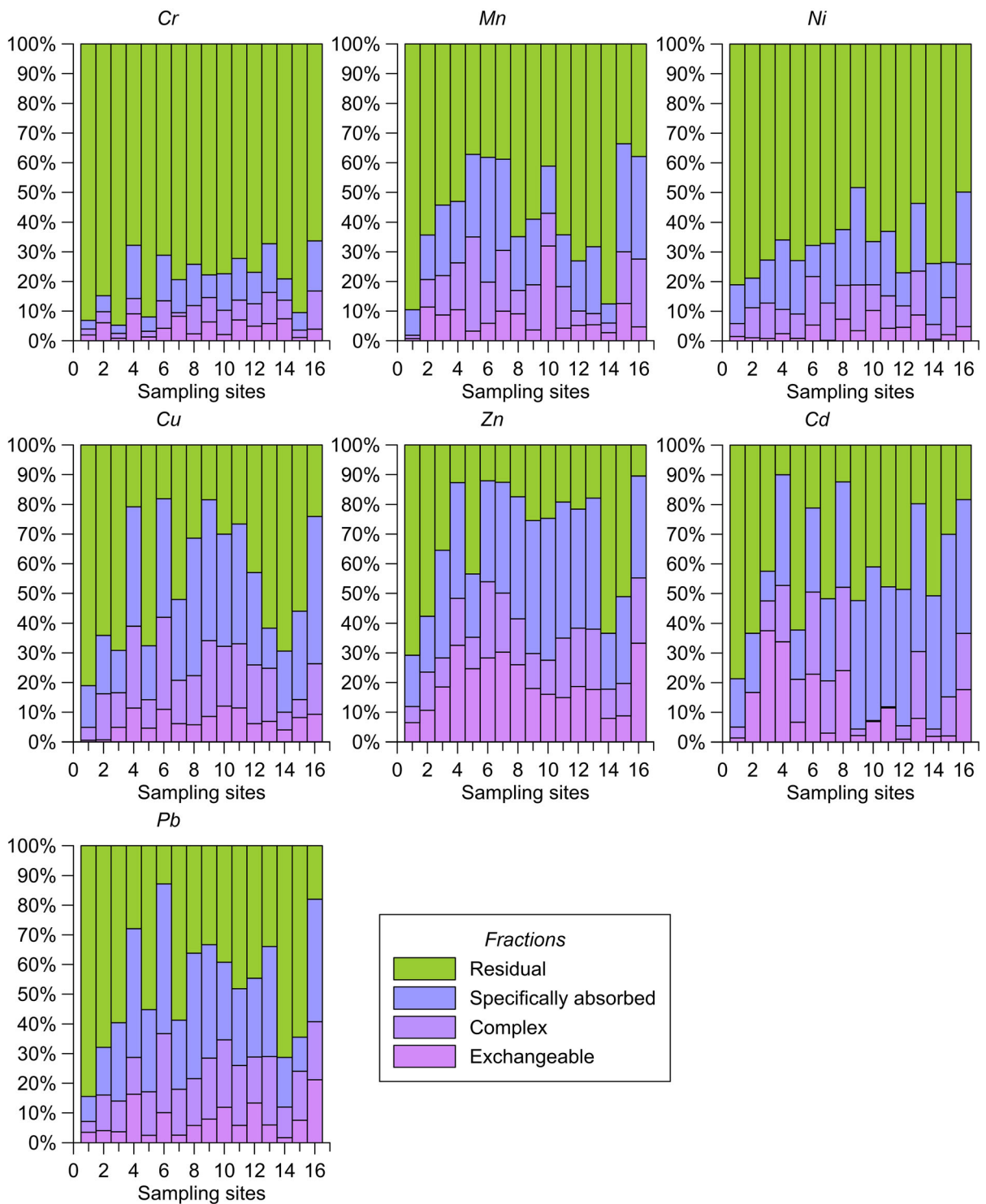


Fig. 3 Partitioning of Cr, Mn, Ni, Cu, Zn, Cd, and Pb in soils from different sampling sites from Lake Atamanskoye

Table 3 Pearson correlations between total PTE content and soils properties

| | Cr | Mn | Ni | Cu | Zn | Cd | Pb | pH | PC | Clay | TOC | CaCO ₃ | Ca ²⁺ | Mg ²⁺ |
|-------------------|--------|--------|--------|--------|--------|---------|---------|--------|--------|--------|--------|-------------------|------------------|------------------|
| Cr | 1.000 | | | | | | | | | | | | | |
| Mn | 0.160 | 1.000 | | | | | | | | | | | | |
| Ni | 0.660* | 0.664* | 1.000 | | | | | | | | | | | |
| Cu | 0.716* | 0.511* | 0.835* | 1.000 | | | | | | | | | | |
| Zn | 0.722* | 0.604* | 0.754* | 0.806* | 1.000 | | | | | | | | | |
| Cd | 0.150 | -0.045 | -0.016 | 0.236 | 0.033 | 1.000 | | | | | | | | |
| Pb | 0.659* | -0.121 | 0.191 | 0.315 | 0.283 | 0.469 | 1.000 | | | | | | | |
| pH | -0.104 | 0.433 | 0.220 | 0.024 | 0.342 | -0.584* | -0.580* | 1.000 | | | | | | |
| PC | 0.311 | 0.085 | 0.207 | 0.099 | 0.140 | 0.245 | 0.156 | -0.127 | 1.000 | | | | | |
| Clay | 0.107 | 0.044 | -0.011 | -0.110 | 0.029 | 0.134 | -0.101 | 0.134 | 0.862* | 1.000 | | | | |
| TOC | 0.561* | -0.169 | 0.109 | -0.051 | 0.086 | 0.105 | 0.698* | -0.306 | 0.323 | 0.213 | 1.000 | | | |
| CaCO ₃ | 0.442 | 0.594* | 0.557* | 0.577* | 0.832* | -0.148 | -0.023 | 0.634* | 0.215 | 0.174 | -0.098 | 1.000 | | |
| Ca ²⁺ | 0.166 | -0.037 | -0.118 | -0.056 | 0.007 | 0.286 | 0.173 | -0.293 | 0.851* | 0.700* | 0.259 | 0.105 | 1.000 | |
| Mg ²⁺ | 0.120 | 0.120 | -0.081 | -0.023 | 0.124 | 0.287 | 0.128 | -0.020 | 0.773* | 0.774* | 0.249 | 0.283 | 0.862* | 1.000 |

*Significant at $p < 0.05$

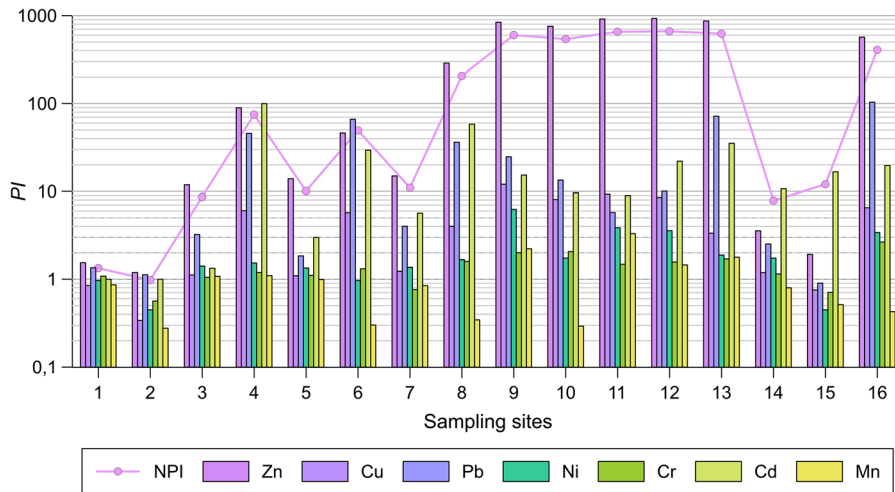


Fig. 4 Single pollution index (PI) and Nemerow pollution index (NPI) of PTEs in soils of Lake Atamanskoye. The dashed lines correspond to the limits of soil contamination classes according to PI values

Table 4 Average content of PTEs (mg/kg) in plant tissues

| Plant species | Cr | Mn | Ni | Cu | Zn | Cd | Pb |
|---|-----------------------------|---------------------------------|-----------------------------|-----------------------------|-------------------------------------|---------------------------------|--------------------------------|
| <i>Phragmites australis</i> (Cav.) Trin. ex Steud. (n = 13) | | | | | | | |
| Root | <u>5.7 ± 1.8</u> 2.7–9.1 | <u>45.3 ± 20.3</u> 21.0–75.0 | <u>2.8 ± 1.1</u> 1.1–5.1 | <u>4.6 ± 0.9</u> 3.4–6.4 | <u>622.6 ± 431.8</u> 30.5–1255.5 | <u>0.33 ± 0.26</u> 0.06–0.88 | <u>14.1 ± 12.7</u> 2.1–44.5 |
| Stem | <u>3.5 ± 1.1</u> 1.4–4.8 | <u>28.3 ± 7.3</u> 18.0–41.0 | <u>1.1 ± 0.5</u> 0.5–1.7 | <u>3.9 ± 1.7</u> 1.3–7.5 | <u>478.1 ± 389.8</u> 24.0–1032.4 | <u>0.16 ± 0.09</u> 0.04–0.36 | <u>5.1 ± 2.9</u> 1.3–11.2 |
| <i>Artemisia austriaca</i> Jacq. (n = 1) | | | | | | | |
| Root | 2.4 | 68.0 | 5.4 | 8.9 | 104.1 | 0.18 | 13.0 |
| Stem | 2.3 | 45.0 | 6.1 | 8.5 | 159.2 | 0.16 | 19.0 |
| <i>Tanacetum vulgare</i> L. (n = 1) | | | | | | | |
| Root | 14.0 | 14.0 | 7.0 | 7.9 | 38.7 | 1.5 | 7.1 |
| Stem | 12.3 | 16.0 | 10.0 | 9.0 | 104.6 | 2.2 | 14.2 |
| <i>Cichorium intybus</i> L. (n = 1) | | | | | | | |
| Root | 2.9 | 35.0 | 4.5 | 15.6 | 55.0 | 2.1 | 2.1 |
| Stem | 1.4 | 22.0 | 3.9 | 13.8 | 63.0 | 1.4 | 2.3 |

The *mean ± SD* is above the line, *min–max* values are below the line, *n* is the number of soil samples

Zn (0.754), and Cu–Zn (0.806). Therefore, it is possible to suggest that these elements (Cr, Ni, Zn, Mn, and Cu) have similar geochemical behaviour within the aquatic landscapes of Lake Atamanskoye. Positive correlations for Pb were observed only with Cr (0.659), while Cd showed no correlation with any of the other metals. At the same time, elements such as Cr and Pb showed positive correlations with TOC,

while for Mn, Ni, Cu, and Zn, the content of CaCO₃ was the only significant soil parameter that affected their geochemical behaviour. These cationogenic elements are not mobile in an alkalic environment and therefore carbonates strongly affect their geochemistry in the soil environment (Kabata-Pendias 2011).

Table 5 Pearson correlations of PTE content in plant tissues

| | Root | | | | | | | Stem | | | | | | |
|------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|-------|
| | Cr | Mn | Ni | Cu | Zn | Cd | Pb | Cr | Mn | Ni | Cu | Zn | Cd | Pb |
| Root | | | | | | | | | | | | | | |
| Cr | 1.000 | | | | | | | | | | | | | |
| Mn | -0.330 | 1.000 | | | | | | | | | | | | |
| Ni | 0.558* | 0.003 | 1.000 | | | | | | | | | | | |
| Cu | -0.055 | -0.063 | 0.514* | 1.000 | | | | | | | | | | |
| Zn | 0.229 | 0.288 | -0.142 | -0.351 | 1.000 | | | | | | | | | |
| Cd | 0.341 | -0.332 | 0.521* | 0.795* | -0.250 | 1.000 | | | | | | | | |
| Pb | 0.356 | -0.101 | 0.165 | -0.085 | 0.283 | -0.074 | 1.000 | | | | | | | |
| Stem | | | | | | | | | | | | | | |
| Cr | 0.945* | -0.286 | 0.604* | -0.001 | 0.042 | 0.394 | 0.129 | 1.000 | | | | | | |
| Mn | -0.369 | 0.914* | 0.113 | -0.057 | 0.172 | -0.431 | -0.040 | -0.313 | 1.000 | | | | | |
| Ni | 0.496 | -0.145 | 0.835* | 0.545* | -0.403 | 0.540* | -0.150 | 0.662* | -0.045 | 1.000 | | | | |
| Cu | 0.110 | 0.024 | 0.641* | 0.941* | -0.274 | 0.730* | -0.072 | 0.168 | 0.072 | 0.659* | 1.000 | | | |
| Zn | 0.188 | 0.334 | -0.111 | -0.305 | 0.956* | -0.214 | 0.068 | 0.066 | 0.203 | -0.310 | -0.221 | 1.000 | | |
| Cd | 0.595* | -0.399 | 0.671* | 0.641* | -0.345 | 0.857* | -0.157 | 0.692* | -0.442 | 0.819* | 0.683* | -0.279 | 1.000 | |
| Pb | 0.421 | -0.035 | 0.661* | 0.251 | -0.056 | 0.088 | 0.437 | 0.459 | 0.167 | 0.674* | 0.369 | -0.080 | 0.303 | 1.000 |

*Significant at $p < 0.05$

Table 6 Pearson correlations between PTE content in plant tissues and total content and fractions of PTEs in soils

| Soil | Stem | | | | | | | | | | | | |
|-------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | Root | | | | | | Stem | | | | | | Pb |
| Cr | Mn | Ni | Cu | Zn | Cd | Pb | Cr | Mn | Ni | Cu | Zn | Cd | |
| Cr _{tot} | 0.413 | 0.005 | 0.118 | -0.259 | 0.771* | -0.218 | 0.599* | 0.162 | 0.005 | -0.216 | -0.185 | 0.652* | 0.226 |
| Cr _{f1} | 0.589* | 0.287 | 0.129 | -0.286 | 0.660* | -0.065 | 0.432 | 0.441 | 0.127 | -0.081 | -0.116 | 0.587* | 0.093 |
| Cr _{f2} | 0.472 | -0.161 | 0.116 | -0.214 | 0.718* | -0.112 | 0.717* | 0.189 | -0.181 | -0.229 | -0.179 | 0.583* | 0.215 |
| Cr _{f3} | 0.453 | -0.076 | 0.041 | -0.286 | 0.753* | -0.105 | 0.774* | 0.181 | -0.129 | -0.324 | -0.271 | 0.574* | 0.165 |
| Mn _{tot} | 0.011 | 0.741* | -0.030 | -0.151 | 0.559* | -0.205 | -0.217 | 0.036 | 0.606* | -0.058 | -0.030 | 0.643* | -0.083 |
| Mn _{f1} | -0.125 | 0.691* | 0.016 | 0.009 | 0.523* | -0.062 | -0.141 | -0.087 | 0.569* | -0.066 | 0.079 | 0.539* | 0.030 |
| Mn _{f2} | -0.143 | 0.844* | 0.051 | -0.082 | 0.336 | -0.246 | -0.136 | -0.142 | 0.767* | -0.088 | 0.033 | 0.341 | -0.141 |
| Mn _{f3} | -0.119 | 0.873* | -0.029 | -0.039 | 0.540* | -0.210 | -0.075 | -0.138 | 0.710* | -0.154 | 0.058 | 0.596* | -0.099 |
| Ni _{tot} | 0.257 | 0.475 | 0.144 | -0.175 | 0.705* | -0.239 | 0.177 | 0.122 | 0.432 | -0.103 | 0.022 | 0.717* | 0.062 |
| Ni _{f1} | 0.238 | 0.178 | -0.104 | -0.279 | 0.953* | -0.232 | 0.283 | 0.031 | 0.090 | -0.359 | -0.196 | 0.919* | -0.029 |
| Ni _{f2} | 0.220 | 0.397 | 0.189 | -0.103 | 0.628* | -0.240 | 0.422 | 0.012 | 0.371 | -0.159 | 0.043 | 0.579* | 0.105 |
| Ni _{f3} | 0.241 | 0.474 | 0.189 | -0.093 | 0.564* | -0.173 | 0.182 | 0.111 | 0.403 | -0.064 | 0.084 | 0.564* | 0.017 |
| Cu _{tot} | 0.209 | 0.309 | -0.110 | -0.223 | 0.828* | -0.220 | 0.314 | 0.031 | 0.269 | -0.320 | -0.067 | 0.742* | 0.004 |
| Cu _{f1} | 0.199 | 0.285 | -0.113 | -0.204 | 0.776* | -0.204 | 0.332 | 0.023 | 0.256 | -0.294 | -0.064 | 0.637* | 0.023 |
| Cu _{f2} | 0.164 | 0.332 | -0.167 | -0.185 | 0.722* | -0.206 | 0.333 | 0.005 | 0.282 | -0.327 | -0.029 | 0.623* | -0.007 |
| Cu _{f3} | 0.216 | 0.283 | -0.024 | -0.178 | 0.748* | -0.193 | 0.371 | 0.022 | 0.275 | -0.289 | -0.020 | 0.642* | 0.008 |
| Zn _{tot} | 0.176 | 0.284 | -0.162 | -0.291 | 0.954* | -0.253 | 0.110 | 0.014 | 0.155 | -0.336 | -0.205 | 0.963* | -0.076 |
| Zn _{f1} | 0.252 | 0.190 | -0.061 | -0.288 | 0.933* | -0.237 | 0.355 | 0.028 | 0.094 | -0.356 | -0.221 | 0.895* | 0.005 |
| Zn _{f2} | 0.184 | 0.280 | -0.161 | -0.298 | 0.926* | -0.235 | 0.171 | 0.023 | 0.145 | -0.338 | -0.242 | 0.935* | -0.051 |
| Zn _{f3} | 0.159 | 0.299 | -0.178 | -0.288 | 0.947* | -0.252 | 0.049 | 0.014 | 0.163 | -0.324 | -0.199 | 0.962* | -0.095 |
| Cd _{tot} | 0.229 | 0.020 | -0.020 | -0.031 | 0.221 | 0.306 | 0.448 | 0.191 | -0.123 | -0.202 | -0.106 | 0.116 | 0.018 |
| Cd _{f1} | 0.139 | 0.051 | -0.021 | -0.081 | 0.052 | 0.207 | 0.422 | 0.133 | -0.029 | -0.172 | -0.154 | -0.083 | 0.014 |
| Cd _{f2} | 0.177 | -0.082 | -0.055 | -0.069 | 0.139 | 0.258 | 0.486 | 0.141 | -0.182 | -0.241 | -0.179 | 0.038 | -0.020 |
| Cd _{f3} | 0.249 | 0.027 | 0.002 | 0.016 | 0.286 | 0.358 | 0.425 | 0.199 | -0.156 | -0.192 | -0.072 | 0.194 | -0.032 |
| Pb _{tot} | 0.351 | -0.129 | -0.003 | -0.152 | 0.435 | -0.057 | 0.919* | 0.098 | -0.193 | -0.303 | -0.202 | 0.252 | -0.187 |
| Pb _{f1} | 0.327 | -0.140 | 0.157 | -0.101 | 0.311 | -0.064 | 0.918* | 0.057 | -0.115 | -0.207 | -0.130 | 0.092 | -0.135 |
| Pb _{f2} | 0.319 | -0.160 | -0.074 | -0.133 | 0.415 | -0.090 | 0.874* | 0.071 | -0.220 | -0.301 | -0.174 | 0.245 | -0.189 |
| Pb _{f3} | 0.333 | -0.155 | -0.020 | -0.128 | 0.369 | -0.045 | 0.939* | 0.087 | -0.196 | -0.297 | -0.175 | 0.174 | -0.180 |

*Significant at $p < 0.05$

Fig. 5 Hierarchical dendrograms showing clustering of sampling sites according to content of PTEs in **a** soils and **b** plant tissues. Ward’s method, 1-Pearson *r* distance. The dashed line represents the critical level of amalgamation

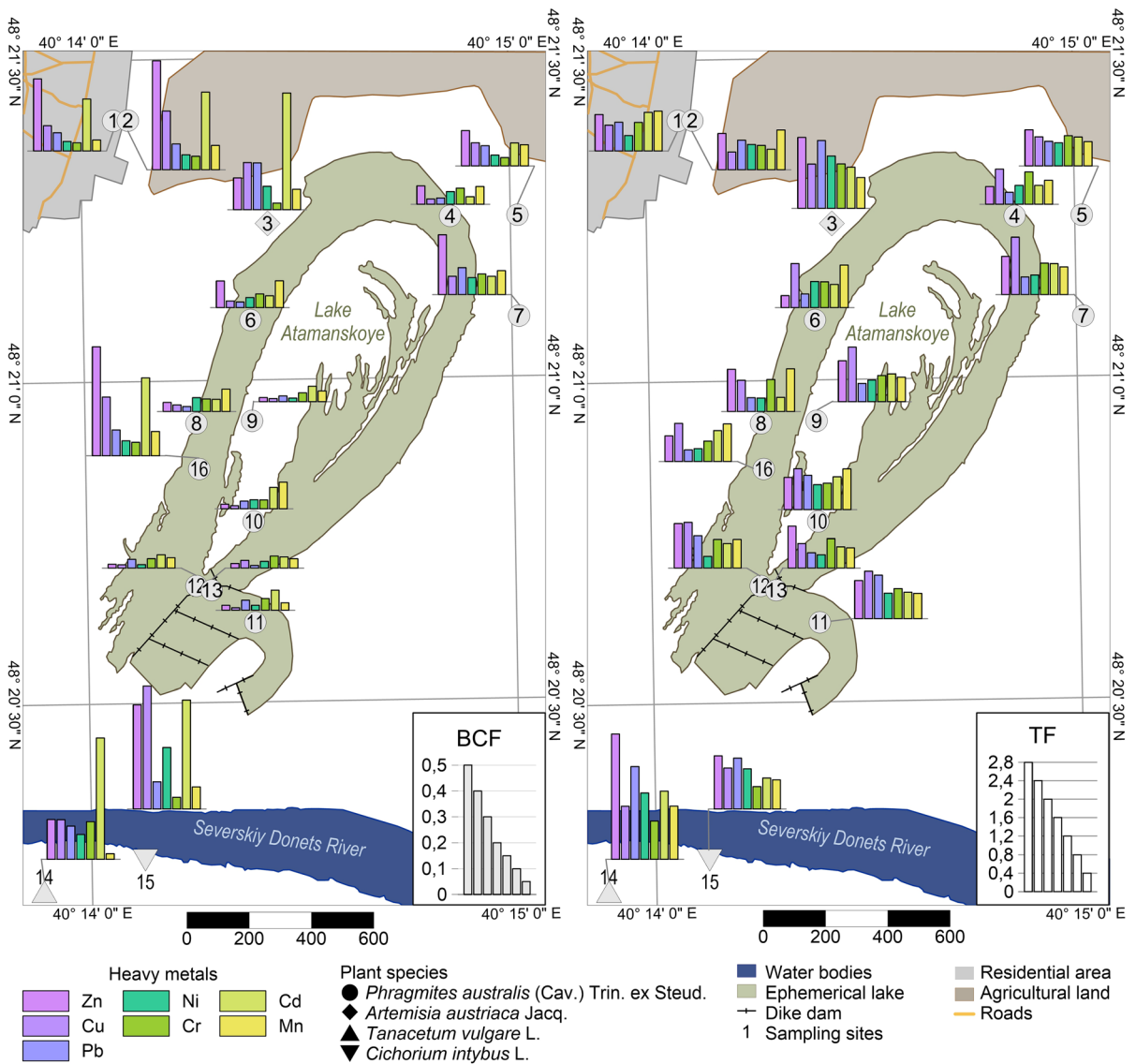
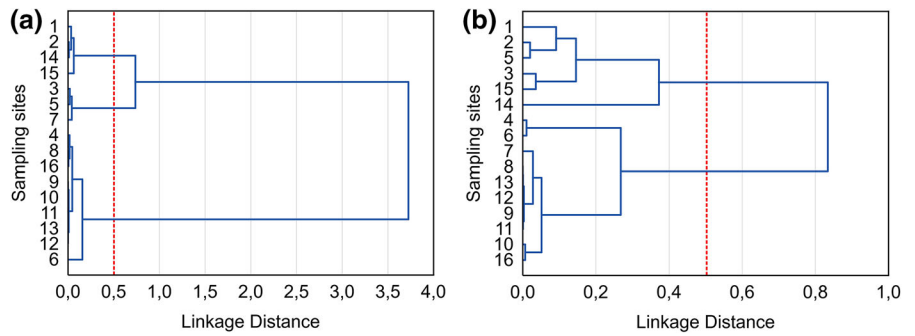


Fig. 6 Bioconcentration factor (BCF) and translocation factor (TF) of PTEs in plant tissues from different sampling sites within Lake Atamanskoye

Soil pollution assessment

Histograms illustrating the single PI and the NPI of PTEs in soils of Lake Atamanskoye and surroundings are presented in Fig. 4. Extremely high PI values for Zn (> 100) were observed in the most polluted *Spolic Technosols*, especially alkaline soils. These soils were also contaminated with Cd ($PI > 10$). PI values higher than 10 but with lower pH values were observed for Cu in *Spolic Technosols* (*Dystric, Fluvic, Toxic*) and *Folic Fluvisols* (*Lomic, Toxic*).

The NPI values for most technogenic or highly transformed soils did not fall below 10. For acidic *Spolic Technosols*, they lie in the range between 10 and 100 and for alkalic *Spolic Technosols* in all studied samples they were much higher than 100.

Accumulation of PTEs in plants and their uptake

Table 4 summarises the data on the accumulation of PTEs in roots and stems of *P. australis*, *T. vulgare*, *C. intybus*, and *A. austriaca*. It is clear that the highest concentration of Zn (up to 1255.5 mg/kg), which is the most significant pollutant related to rayon industry effluents, was observed in the roots of *P. australis*, almost 40 times higher than in the root systems of similar plants growing in unpolluted or slightly polluted areas. It is also noted that the concentrations of the metals in the roots of *P. australis* were higher than in the stems. Although the sample sets for different plant species were quite different, the results suggest that significant variability exist in the ability of various plants to accumulate different metals.

Table 5 presents the Pearson correlations of PTEs in plant tissues. The relationships between concentrations of individual metals in roots and stems are revealed for most of the metals, with exception of Pb. For the elements Cr, Mn, Cu, and Zn, there are very strong positive correlations ($p < 0.05$). The analysis revealed that for the plant species studied, there were medium and strong positive correlations between the following pairs of metals in roots: Cr–Ni (0.558), Ni–Cu (0.514), Ni–Cd (0.521), and Cd–Cu (0.795). In the stems of the plants, correlative pairs presented these values: Cr–Ni (0.662), Cr–Cd (0.692), Ni–Cu (0.659), Ni–Cd (0.819), Pb–Ni (0.674), and Cu–Cd (0.683), indicating strong differences in the bioaccumulation of metals in different plant organs. It is interesting to note that the concentration of Zn in roots only

correlated with the concentrations of this element in the stems, which probably indicates that the biogeochemistry of this element under conditions of extreme soil pollution is altered.

Results of Pearson correlations between the content of PTEs in plant tissues and the total content and fractions of PTEs in the soils are presented in (Table 6). Based on the results of this statistical analysis, we suggest that there are medium to very strong positive correlations between the content of Cr, Mn, Ni, Cu, and Zn, as well as the forms and concentrations of Zn in the roots and stems. For Mn, the most significant relations were observed between the concentrations of this element and its forms in soils, roots, and stems. The intensity of bioaccumulation of Pb in roots showed positive correlations with the concentration of this metal and its forms and total Cr content, as well as specifically absorbed and complex forms. The content of exchangeable forms of Cr was the most significant factor influencing its accumulation in the roots.

The hierarchical dendrograms show clustering of sampling sites according to the PTE content in soils (Fig. 5a) and plant tissues (Fig. 5b). It is clear that the clusters allocated according to these parameters are very similar. The first cluster includes slightly polluted *Fluvisols* and background soils, and the second cluster comprises *Technosols* and heavily polluted *Fluvisols*.

Figure 6 presents the map illustrating the spatial distribution of bioaccumulation factors of PTEs in plant tissues from different sampling sites within Lake Atamanskoye. It is clear that for most of the heavily polluted natural and technogenic soils, the BCF values of Cu, Pb, Ni, Cr, and Mn were rather low. The BCF values of all PTEs did not exceed 1 at any of the sites, which indicates that the soil is the main source of PTEs in plants, and the barrier functions of the root system are manifest regardless of the plant species. In acidic *Technosols* and *Fluvisols*, these values were higher.

Values for the TF vary by plant species. *T. vulgare* are tolerant to PTEs included in this study ($TF > 1$) except Cr, and *C. intybus* are tolerant to Zn and Pb and grow on weakly contaminated *Folic Fluvisols*. *A. austriaca* shows relatively high BCF values for Zn (1.5), Pb (1.5), and Ni (1.1), although it grows at the more contaminated site 3. *P. australis* demonstrates higher plant defence potential for all PTEs ($TF < 1$ at all sites except for Cu at sites 7 and 9). Thus, *P. australis* can be used as a natural phytostabiliser for

remediation of highly contaminated soils in the study area.

Implication for management and remediation of soils and sediments of Lake Atamanskoye

Our studies show that extremely high levels of PTEs in the area of former Lake Atamanskoye have led to the geochemical transformation of floodplain soils and vegetation, and created significant environmental risks for the entire lower Don Basin. Although it is obvious that the current water body is practically drained, seasonal fluctuations of water level and flooding can restore the lake, as it did several times during the 2000s and 2010s. Such conditions would increase leaching of PTEs and contribute to their migration into the Seversky Donets.

Another important point concerns the presence of two contrasting types of technogenic soils within the study area. Alkalic *Technosols* contain the highest concentrations of PTEs, while acidic technogenic soils are characterised by higher proportions of more mobile forms with a higher potential for bioaccumulation. Therefore, remediation and management strategies should offer different solutions for different parts of the former lake area that account for differences in pH values and carbonate content, which significantly affect metal sorption (Piri et al. 2019). Such widespread methods as phytostabilisation and phytoextraction are often used in metal-rich environments (Boi et al. 2020) and are more suitable for acidic soils, while chemical or physical are better suited for use with alkalic *Technosols*.

Conclusion

The results of this study show that long-term pollution of Lake Atamanskoye resulted in significant geochemical transformation of adjacent soils and floodplain vegetation. *Spolic Technosols (Fluvic, Toxic)*, *Spolic Technosols (Dystric, Fluvic, Toxic)* and *Folic Fluvisols (Lomic, Toxic)* represent the soils of the drained water body and its surroundings and differ significantly from the background soils in terms of their physical and chemical properties.

Technogenic soils of Lake Atamanskoye can be divided into two groups based on the pH values and the presence of carbonates. The concentrations of most of

the metals in both *Spolic Technosols* and *Fluvisols* were strongly affected by rayon industry effluents and are extremely higher than regional geochemical background levels and the world geochemical baseline values by several orders of magnitude. The content of carbonates and accordingly the pH values strongly affect the concentrations of metals, as well as the proportion of their various forms. A higher proportion of exchangeable and complex forms were observed for acidic soils, while for alkalic soils, the composition of metal fractions was dominated by specially absorbed and residual forms.

A higher intensity of bioaccumulation was characteristic of contaminated soils with low pH values, so it is possible to suggest that elements such as Ni, Zn, Mn, and Cu are characterised by similar geochemical behaviour under conditions of extreme pollution, and the concentrations of these metals in soils have medium to strong positive correlations with CaCO₃ content. Metals such as Cr and Pb were affected by TOC, and Cd demonstrated no significant relationships with any of the metals or soil parameters. Extremely high contents of PTEs, especially Zn in soils of Lake Atamanskoye, as well as the high proportion of their mobile forms in soils with low pH values, are significant risk factors for the environmental health of the Don basin. Leaching of metals and their migration into water bodies, as well as significant flooding events, can lead to the pollution of downstream territories. In this circumstance, Lake Atamanskoye requires special measures to monitor and reclaim the territory for the benefit of the people and the environment.

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