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Environmental and human health risk assessment of potentially toxic elements in soils around the largest coal-fired power station in Southern Russia

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Abstract The combustion of solid fuel at power plants pollutes adjacent areas with potentially toxic elements (PTEs), which increases risks to public health in the vicinity of these facilities. The proposed paper presents the results of a geochemical study of PTEs (Cr, Mn, Ni, Cu, Zn, Cd, and Pb) contamination in the vicinity of Novocherkassk Power Plant (NPP) as it relates to environmental and human health risks. The impact zone of NPP is pronounced for a distance of approximately 7 km northwest of the enterprise—the second largest coal power plant in Southern Russia. Data from monitoring sites lead us to conclude that spatial patterns of soil pollution are strongly influenced by the peculiarities of local atmospheric circulation, while the characteristics of soils within the study area play a secondary role. The highest levels of PTEs and their exchangeable forms exceed both regional background and sanitary and hygienic standards within a radius of 3 km to the west of the plant, which corresponds to a zone of soils contaminated with Cr, Ni, Cu, Zn, Cd, and Pb. The carcinogenic risk to human health slightly exceeds the permissible standard of 1×10^{-6} for soils in close vicinity of the enterprise due to the potential human intake of Ni, Cd, and Pb. The results of the health risk assessment indicate no noncarcinogenic risks for adults, while for children, they are low.

Keywords Soil pollution · Trace elements · Coal power plant · Environmental risk assessment · Carcinogenic risk · Noncarcinogenic risk

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Introduction

Production of energy at power plants is one of the most significant sources of environmental pollution, especially when solid fuel such as coal is used. Combustion of coal leads to the emissions of substances such as nitrogen oxides (NO_x), carbon monoxide (CO), sulfur dioxide (SO_2), greenhouse gases and dust which contains a number of potentially toxic elements (PTEs)—Cr, Mn, Ni, Cu, Zn, Cd, and Pb (Ćujić et al. 2016; Huang et al. 2017; Piersanti et al. 2018; Linnik et al. 2019). Organic and inorganic pollutants

resulting from solid fuel combustion accumulate in soils surrounding such enterprises. These sources of chemical pollution are often located in areas with high population density (Konstantinova et al. 2019) and, therefore, pose a potential danger to public health.

In the ecological and geochemical assessment of soils, three main approaches are used: comparing the chemical content of the soils to a global geochemical background (GB), a regional geochemical background (RB) and with legislatively established sanitary and hygienic standards (MU 2.1.7.730-99 1999; Chernova and Beketskaya 2011; Kabata-Pendias 2011; D'yachenko and Matasova 2016; Barsova et al. 2019; Linnik et al. 2019; Rahman and Begum 2019). Clarkes of elements in the upper continental crust and the world average content of elements in soils are usually used as global reference standards to assess the degree of technogenic geochemical transformation of natural environments (Chernova and Beketskaya 2011; Kasimov and Vlasov 2015). Reference RB provides an understanding of the average content of chemical elements in soils at sites, which are characterized by similar geological background and uniform in terms of landscape structure and do not have anthropogenic sources of elements (Reimann and Garrett 2005). Exceeding RB indicates the degree of soil pollution (Adriano 2001; Kowalska et al. 2018). Maximum permissible concentrations (MPCs) and tentative allowable concentrations (TACs) of chemicals in soils are established as the main criteria for hygienic assessment of chemical pollution in soils in Russia (GN 2.1.7.2041-06 2006; GN 2.1.7.2511-09 2009). Exceeding the standard values indicates soil pollution, which is dangerous not only for human and animal health, but also for the quality of the environment (MU 2.1.7.730-99 1999).

Human health risk assessment is based on a model developed by the US Environmental Protection Agency (US EPA 1989). The chronic effect of high doses of PTEs on the human body is manifest in the occurrence of general toxic effects. Chronic exposure of Mn leads to cardiac and liver disfunction, permanent neurodegenerative disorder, decreased fertility, and increased fetal abnormalities (Crossgrove and Zheng 2004). Long-term excessive Cr(III) intake reduces fertility in women (Gad 2014a), and Zn causes sideroblastic anemia, hypochromic microcytic anemia, leukopenia, lymphadenopathy, neutropenia, hypocupremia, and hypoferremia (Nriagu 2011).

Chronic ingestion of high doses of Cu leads to liver cirrhosis, neurological abnormalities, hemolytic anemia, and decline in memory and cognition (Gad 2014b); Cd affects the gastrointestinal, liver, heart, kidney, and reproductive system (Eisler 2000). Skin contact with certain Cr(III) and Ni compounds can cause allergic reactions (Gad 2014a). Assessment of general toxic risks involves the separation of recipients into age groups, since children differ from adults in their vulnerability to environmental pollutants because of toxicodynamic differences (e.g., exposures that occur during periods of enhanced susceptibility) and/or toxicokinetic differences (i.e., differences in absorption, metabolism, and excretion) (US EPA 2011). In this regard, pollution of soils with Pb is of particular concern since this element not only negatively affects the central nervous system, kidney, and hematopoietic system, but also causes decreased intelligence quotient, decreased stature and growth, and impaired hearing acuity, encephalopathy, memory loss in children (Youravong 2011). A number of PTEs and their compounds, including Cr(VI), Ni, Cd, and Pb, are classified as carcinogenic to humans (IARC 2019). Carcinogenic effects can occur throughout a person's life, since any amount of a substance can cause malignant changes (US EPA 1989). Thus, the system for human health risks assessment makes it possible to account for the carcinogenic and general toxic effects of metals or other substances entering the bodies of individuals of different age groups through various pathways.

With an installed electric capacity of 2258 MW (Gazprom 2020), the Novocherkassk Power Plant (NPP) is the top electric energy producer in Southern Russia. This facility is located in the vicinity of one of the largest cities in the Rostov Region, Novocherkassk, with a population of 167,000 people. Among the major cities in the region, Novocherkassk is characterized by the maximum level of atmospheric pollution. Emissions from vehicles and a variety of industrial enterprises within this settlement, including NPP (Minprirody of the Rostov Oblast 2019), have been estimated at 6.47 Kt of particulate emitted per year. Comprehensive monitoring studies of soil cover and associated natural systems show an increase in the levels of PTEs in soils and plants within the area surrounding the NPP (Minnikova et al. 2017; Chaplygin et al. 2018, 2019; Burachevskaya et al. 2019; Linnik et al. 2019). However, no health risk studies

have been carried out in the impact zone of this enterprise, although residents of Novocherkassk risk exposure to high levels of PTEs in the environment which may lead to a variety of health-related issues in this population as compared to average regional rates (Rospotrebnadzor of the Rostov Oblast 2019).

In this study, we considered the ecological and human health risks of Cr, Mn, Ni, Cu, Zn, Cd, and Pb typical of coal-fired power plants emission (Tang et al. 2013; Huang et al. 2017; da Silva Junior et al. 2019) in soils of the impact zone of NPP. In accordance with the standards for pollution control and state-of-soil forecasts in Russia, the PTEs under consideration were classified into the following classes: Zn, Cd, and Pb—high hazard; Cr, Ni, and Cu—moderate hazard; and Mn—low hazard (GOST 17.4.1.02-83 1984). The main objectives of the present study were: (1) to characterize the spatial distribution of selected PTEs in soils affected by NPP; (2) to assess potential environmental risks of PTEs within the territory; and (3) to evaluate possible carcinogenic and noncarcinogenic risks related to PTEs in soils around NPP.

Materials and methods

Study area and soil sampling

The present study was conducted in the impact area of NPP (N47°24′00″, E40°13′54″), which occupies the valleys of the Tuzlov and Aksay Rivers and the Aksay upland in the Rostov Region of Russia, 35 km northeast of Rostov-on-Don (Fig. 1). The study area is characterized by a temperate continental climate; east and northeast winds prevail (Kazakov 2019). The

local atmospheric circulation is modified under the influence of local topographic features: Winds that penetrate from the east into the valleys of the Aksay and Tuzlov rivers (1–8 m high) meet a natural orographic barrier in the form of the Aksai upland (up to 106 m).

Field studies were performed at 12 monitoring sites laid along the radii emanating from the NPP chimneys in various directions. The sites were located in the near-source influence zone (up to 3 km) and at greater distances (from 3 to 20 km) downwind (Fig. 1). This site selection method is widely used to determine the spatial distribution of pollutants in the impact areas of power plants (Tang et al. 2013; Noli and Tsamos 2016; Huang et al. 2017; da Silva Junior et al. 2019) and other large enterprises. This arrangement allowed us to account for the orographic features in the area, the nature of atmospheric circulation, and the occurrence of other potential sources of pollution.

Soils from the monitoring sites were classified according to the World Reference Base of Soil Resources (IUSS Working Group WRB 2015). Floodplains and high river terraces occupied by *Haplic Chernozem* formed on loess-like loams under the steppe vegetation (sites 1, 4–5, 7, 9–12). *Stagnic Phaeozem* occupies floodplain terraces and lower slopes covered with wet grasslands under conditions of waterlogging (sites 3, 6, 8). *Stagnic Phaeozem* has similar physical–chemical properties to that of *Haplic Chernozem* (Table 1) in that both are slightly to moderately alkaline (pH values 7.3–8.3) with loam and clay loam texture. However, *Stagnic Phaeozem* has a higher content of clay fraction, total organic carbon (TOC), and cation exchange capacity (CEC) as compared with *Haplic Chernozem*. Coarse-textured

Fig. 1 Simplified map of study area, showing distribution of land use types, and location of sampling points

Table 1 Descriptive statistics of physical–chemical properties of studied soils within the NPP impact area (g/kg, except for CEC in cmol(+)/kg and pH)

Soil	N	pH	TOC	CaCO₃	CEC	Clay
Haplic Chernozems	8	<u>7.7</u> 7.3–8.0	<u>21</u> 11–26	<u>6</u> 1–9	<u>35.0</u> 25.0–42.0	<u>289</u> 166–359
Stagnic Phaeozems	3	<u>7.7</u> 7.5–7.9	<u>28</u> 24–35	<u>9</u> 8–9	<u>44.0</u> 41.0–46.0	<u>383</u> 345–426
Calcaric Fluvic Arenosol	1	<u>7.5</u>	<u>9</u>	<u>5</u>	<u>15.0</u>	<u>24</u>

Mean values are underlined. *N* number of soil samples, *TOC* total organic carbon, *CEC* cation exchange capacity

Calcaric Fluvic Arenosol (site 2) occurs on sandy alluvial sediments in the central floodplain (site 2).

Soil samples were collected in June 2019 using an envelope method (GOST 17.4.4.02-2017 2018) from the surface soil horizon (0–20 cm deep). The soil samples were air-dried, mixed, ground, and passed through a 1-mm sieve (Vorobyova 2006).

Analytical methods

The particle size analysis was conducted using the pipette method with pyrophosphate procedure of soil preparation (Soil Survey Staff 2011) to obtain total clay fraction (particles < 0.002 mm). The content of total organic carbon in soils was determined using the dichromate oxidation method according to Tyurin (Vorobyova 2006), the pH was measured by potentiometry in the supernatant suspension of a soil and water in a ratio of 1:5 (ISO 10390:2005 2005), CaCO₃ was determined by acid neutralization, and CEC was analyzed with 1.0 mol/L NH₄OAc after soil saturation with 0.5 mol/L BaCl₂, pH 6.5 (Vorobyova 2006).

The total concentrations of Cr, Mn, Ni, Cu, Zn, Cd, and Pb were determined by X-ray fluorescence analysis using a Spectroscan MAX-GV spectrometer (Spectron, Russia) (OST 10-259-2000 2001), and the content of exchangeable forms extracted from the soil by an ammonium acetate buffer solution with pH 4.8 and soil/solution ratio of 1:10 (extraction time was 18 h) (Minkina et al. 2018) was determined by atomic absorption spectrophotometry (AAS) (KVANT 2-AT, Kortec Ltd, Russia) (RD 52.18.289-90 1990). All laboratory tests were performed in triplicate. The accuracy of element determination was verified using duplicates, reagent blanks, and state standard reference samples (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; OST 10-259-2000 2001).

Descriptive statistics were calculated with STA-TISTICA 12 StatSoft (USA) package. Data analysis and visualization were conducted using Microsoft Office, and Grapher 11 Golden Software (USA). Maps were generated using Surfer 12 Golden Software (USA).

Calculation of pollution indices

Geochemical features of soils were determined by calculating the concentration coefficient (CC) as follows:

$$CC = \frac{C_i}{GB}, \tag{1}$$

where C_i is the total content of metal i in a soil sample and GB is the upper continental crust (UCC) content of metal or world soil average (Table 2). Values of CC from 1.0 to 2.0 correspond to near-Clarke nonhazardous contents of elements within the range of natural variation, while values above 2.0 indicate anthropogenic impact on the concentration of elements in the soil (Kasimov and Vlasov 2015).

Various indicators of environmental quality based on a comparison of the content of elements in the soils studied herein with RB were used to assess potential soil pollution (Kowalska et al. 2018). Pollution levels of PTEs in the soils of the NPP impact area were evaluated using 1) the geoaccumulation index (I_{geo}), 2) the single pollution index (PI), and 3) the Nemerow

Table 2 Geochemical background values and permissible concentrations (mg/kg) used for pollution assessment

Value	Cr	Mn	Ni	Cu	Zn	Cd	Pb	References
UCC	92.4	770	50	39	75	0.64	17	Grigoriev (2009)
World soil average	59.5	488	29	38.9	70	0.41	27	Kabata-Pendias (2011)
RB	90.5	800.6	42.5	43.8	71.3	0.3*	22.2	Mandzhieva et al. (2017) and *Minkina et al. (2017)
TAC								
Sandy soils	64**	1500***	20	33	55	0.5	32	GN 2.1.7.2511-09 2009; ** CCME 1999; *** GN 2.1.7.2041-06 2006
Loamy soils (pH > 5.5)			80	132	220	2	130	
MPC	6.0	140	4	3	23		6	GN 2.1.7.2041-06 2006

UCC upper continental crust, *RB* regional geochemical background, *TAC* tentative allowable concentration (total content), *MPC* maximum permissible concentration (exchangeable fraction)

pollution index (NPI). The I_{geo} introduced by Müller (1986) is widely used to assess soil pollution by individual elements (Ćujić et al. 2016; Huang et al. 2017; da Silva Junior et al. 2019); its main advantage is to reduce the influence of lithogenic variability in element contents. The equation is as follows:

$$I_{geo} = \log_2\left(\frac{C_i}{1.5RB}\right), \tag{2}$$

where C_i is the total content of metal i in a soil sample and RB is the regional background value (Table 2). Müller classified seven levels based on I_{geo} values (Müller 1986): class 0—unpolluted (≤ 0); class 1—unpolluted to moderately polluted (0–1); class 2—moderately polluted (1–2); class 3—moderately to highly polluted (2–3); class 4—highly polluted (3–4); class 5—highly to extremely high polluted (4–5); class 6—extremely high polluted (> 5).

The pollution index (PI) is the simple ratio of the element content to the RB as expressed by:

$$PI = \frac{C_i}{RB}, \tag{3}$$

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

The Nemerow pollution index (NPI) was used for a comprehensive assessment of soil pollution by all of the elements studied, regardless of their quantity (Nemerow 1974). The equation is as follows:

$$NPI = \sqrt{\frac{\left(\frac{1}{n}\sum_{i=1}^{n} PI_i\right)^2 + PI_{max}^2}{2}}, \tag{4}$$

where PI_i is the calculated value of the pollution index for the ith 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 hygienic and epidemiological danger of soil pollution by individual elements was evaluated based on the index of danger (ID) (MU 2. 1.7.730-99 1999), calculated as:

$$ID = \frac{C_i}{C_p} \tag{5}$$

where C_i is the total concentration (*tot*) or exchangeable fraction (*exc*) of the ith metal in a soil sample and C_p is the TAC used for assessment of total metal content taking into account the soil texture and pH, or the MPC for the content of exchangeable fraction (Table 2). Since the permissible total concentration of Cr in soils in Russia has not been defined, Canadian soil quality guidelines for total Cr in agricultural soils were used (CCME 1999). The classification of soil contamination using ID, as adapted from (MU 2. 1.7.730-99 1999), was as follows: clean (≤ 0.75), low pollution (0.75–1.0), moderate pollution (1–2), strong pollution (2–3), and very strong pollution (> 3).

The complex soil pollution index (SPI) defined as follows:

$$\text{SPI} = \frac{\sum \text{ID}_i}{n}, \tag{6}$$

According to Bogdanov (2012), soils can be classified into three categories based on SPI values: clean (< 0.75), problem (0.75–1.0), and polluted (> 1.0).

Human health risk from PTEs in soils

Human health risk assessment is a process made up of four basic steps: data collection and analysis, toxicity assessment, exposure assessment, and risk characterization (US EPA 1989). Geochemical data from the soils were collected and analyzed to determine the levels and spatial distribution of Cr, Mn, Ni, Cu, Zn, Cd, and Pb in soils from the NPP impact area.

Toxicity assessment is a quantitative estimation of the likelihood of adverse effects occurring in humans at different exposure levels to contaminants (US EPA 1989). The reference dose (RfD, a noncarcinogenic threshold) and the cancer slope factor (SF, a carcinogen potency factor) are two important toxicity indices used. The values of RfD and SF for oral intake were established by the US EPA and other regulators based on toxicological studies; the rest are determined by calculation (Table 3).

The purpose of exposure assessment is to measure or estimate the intensity, frequency, and duration of human exposures to PTEs through ingestion (ing), inhalation (inh), and dermal (derm) contact by adults and children six years old and younger (US EPA 1989). In order to assess the general toxic effects of soil metals, average daily dose (ADD) was calculated

for three exposure pathways for both age groups according to the following formulas:

$$\text{ADD}_{\text{ing}} = \frac{C_i \times \text{IRs} \times \text{FI} \times \text{EF} \times \text{ED} \times \text{CF}}{\text{BW} \times \text{AT}}, \tag{7}$$

$$\text{ADD}_{\text{derm}} = \frac{C_i \times \text{SA} \times \text{AF} \times \text{ABS}_d \times \text{EF} \times \text{ED} \times \text{CF}}{\text{BW} \times \text{AT}}, \tag{8}$$

$$\text{ADD}_{\text{inh}} = \frac{C_i \times \text{IRa} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT} \times \text{PEF}}, \tag{9}$$

Since carcinogenic risks are caused by long-term exposure to carcinogenic elements, the lifetime average daily dose (LADD) for each of the pathways of entry was calculated as follows (Asante-Duah 2017):

$$\text{LADD}_{\text{ing}} = \frac{C_i \times \text{FI} \times \text{EF} \times \text{CF}}{\text{LT}} \times \left(\frac{\text{ED}_c \times \text{IRs}_c}{\text{BW}_c} + \frac{\text{ED}_a \times \text{IRs}_a}{\text{BW}_a} \right), \tag{10}$$

$$\text{LADD}_{\text{derm}} = \frac{C_i \times \text{ABS}_d \times \text{EF} \times \text{CF}}{\text{LT}} \times \left(\frac{\text{SA}_c \times \text{AF}_c \times \text{ED}_c}{\text{BW}_c} + \frac{\text{SA}_a \times \text{AF}_a \times \text{ED}_a}{\text{BW}_a} \right), \tag{11}$$

$$\text{LADD}_{\text{inh}} = \frac{C_i \times \text{EF}}{\text{LT} \times \text{PEF}} \times \left(\frac{\text{IRa}_c \times \text{ED}_c}{\text{BW}_c} + \frac{\text{IRa}_a \times \text{ED}_a}{\text{BW}_a} \right), \tag{12}$$

The definition, units, and reference values for all parameters used in the above equations are listed in Table 4.

Noncarcinogenic hazards are characterized by a term called the hazard quotient (HQ). The HQ is a

Table 3 Reference doses (RfD, in mg/kg/day) and cancer slope factors (SF, in kg/day/mg) for PTEs

Element	RfD$_{\text{ing}}$	RfD$_{\text{derm}}$	RfD$_{\text{inh}}$	SF$_{\text{ing}}$	Sf$_{\text{derm}}$	SF$_{\text{inh}}$	References
Cr(III)	1.5	3.8E−02	1.4E−03				ATSDR (2019) and US EPA (2019)
Mn	1.4E−01	8.4E−03	0.4E−01				US EPA (2019)
Ni	1.1E−02	4.4E−04	2.6E−05			0.84	ATSDR (2019), OEHHA (2019) and US EPA (2019)
Cu	1.0E−02	2.0E−03					ATSDR (2019)
Zn	0.3	6.0E−02					US EPA (2019)
Cd	1.0E−03	5.0E−05	2.9E−06			6.3	ATSDR (2019) and US EPA (2019)
Pb	3.6E−03	7.2E−04		8.5E−03	4.3E−02	4.2E−02	RIVM (2001) and OEHHA (2019)

Subscripts indicate the entry paths of elements: *ing* ingestion, *derm* dermal contact, *inh* inhalation

Table 4 Exposure parameters used for the health risk assessment

	Parameter	Unit	Children	Adults	References
ABS_d	Dermal absorption factor	Unitless	Cr and Ni 0.02; Mn, Cu, and Zn 0.01; Cd 0.001; Pb 0.034		US EPA (2002) and OEHHA (2012)
AF	Soil adherence factor	mg/cm^2	0.2	0.07	US EPA (2014)
AT	Average time	days	$ED_c \times 365$	$ED_a \times 365$	US EPA (2014)
BW	Body weight	kg	15	80	US EPA (2014)
CF	Conversion factor	kg/mg	1×10^{-6}		US EPA (1989)
ED	Exposure duration	years	6	20	US EPA (2014)
EF	Exposure frequency	days/ year	350		US EPA (2014)
FI	Fraction ingested	Unitless	1		US EPA (1989)
IRa	Inhalation rate	m^3/day	8.1	15.6	US EPA (2011)
IRs	Ingestion rate	mg/day	200	100	US EPA (2014)
LT	Lifetime	days	365×70		US EPA (2014)
PEF	Particulate emission factor	m^3/kg	1.32×10^9		US EPA (2011)
SA	Skin surface area	cm^2	2373	6032	US EPA (2014)

unitless number that expresses the probability of an individual suffering an adverse effect from exposure to environmental hazards (US EPA 1989). It is defined as the quotient of ADD, which is referred to as the RfD of a specific PTE as:

$$HQ = \frac{ADD}{RfD}, \tag{13}$$

The cumulative noncarcinogenic risk of the k number of metals for all pathways is expressed as the Hazard Index (HI) (US EPA 1989):

$$HI = \sum_{k=1}^{n} HQ_k$$
$$= \sum_{k=1}^{n} \left(\frac{ADD_{ing}}{RfD_{ing}} + \frac{ADD_{derm}}{RfD_{derm}} + \frac{ADD_{inh}}{RfD_{inh}} \right)_k, \tag{14}$$

where HQ_k is the hazard quotient of PTE k. According to Lemly (1996), guidelines for interpreting HQ and HI are: no hazard (< 0.1), low hazard (0.1–1.0), moderate hazard (1.1–10), and high hazard (> 10).

Carcinogenic risks were estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogen. The equation for calculating the excess lifetime cancer risk (CR) is:

$$CR = LADD \times SF, \tag{15}$$

The total cancer risk (TCR) for an individual is calculated from the contribution of k number of PTEs for all pathways using the following equation:

$$TCR = \sum_{k=1}^{n} CR_k = \sum_{k=1}^{n} \left(LADD_{ing}SF_{ing} + LADD_{derm}SF_{derm} + LADD_{inh}SF_{inh} \right)_k, \tag{16}$$

According to US EPA (1989), the value of 1×10^{-6} is considered as the maximum acceptable level of carcinogenic target risk. If both CR and TCR are less than 1×10^{-6}, they are negligible, while values above 1×10^{-4} are considered unacceptable by most of the international regulatory agencies (Guney et al. 2010).

Results and discussion

Levels and spatial distribution of PTEs in soils

The distribution of the total concentrations of Cr, Mn, Ni, Cu, and Zn in soil samples from the study sites was uniform (CV $< 33\%$), and the differences between the average and the median were insignificant (Table 5). At the same time, a wide scatter of values was

observed for the total contents of Cd and Pb and the exchangeable forms of all the elements, especially Cd (CV 114.3%), which indicates strong spatial heterogeneity of PTEs within the soils of the study area. Color dot maps (Fig. 2) show the trends in spatial distribution of PTEs across the study area. In general, at a distance of 1 km on the windward side of the facility, relatively low concentrations of the studied metals were observed in soil from sites 11, 12, and 1, while maximum concentrations of PTEs were characteristic of sites 4 and 5 located 2 km west of the NPP chimneys, in the immediate vicinity of the NPP ash dump (Fig. 2). The highest levels of PTEs in these soils can be explained by the transfer of dust from the ash dumps by prevailing winds (Pandey 2015; Krechetov et al. 2019; Konstantinov et al. 2020). To the north and northwest (sites 6 and 7), some distance from the source, concentrations of both total and exchangeable forms of PTEs in soils decreased by approximately 1.5 times.

A decrease in content of PTEs persists moving westward away from the source (Fig. 2). Inconsistency with the general trend is typical for the soil at site 2, despite being located leeward of the impact zone. The soil at site 2 is characterized by low concentrations of PTEs and their exchangeable forms. Perhaps this feature is due to the fact that the soils at site 2 are *Calcaric Fluvic Arenosol*, characterized by a coarse texture and low TOC and CEC, which probably contributes to the poor ability of this soil type to accumulate PTEs (Adriano 2001; Kabata-Pendias 2011). A slight increase in the concentrations of total and exchangeable forms of almost all the PTEs was

Fig. 2 Spatial distribution of total and exchangeable Cr, Mn, Ni, Cu, Zn, Cd, and Pb in soils of the NPP impact area ▶

observed in soils from site 8, located at a sufficient distance from NPP (about 7 km). The soil at this site is *Stagnic Phaeozem*, the upper horizon of which is characterized by the highest TOC value (35 g/kg) and a higher content of clay fraction (378 g/kg) in comparison with the other soils (Table 1), which can lead to significant accumulation of PTEs. On the other hand, elevated concentrations of total and exchangeable forms of PTEs at site 8 soils, despite its significant distance from NPP, can be explained by the orography of the territory under consideration.

It is clear that the metals content in soils decreases sharply at sites located west of the Tuzlov River (Fig. 2), while signs of atmospheric pollution are well pronounced within the river valley (site 8). A similar pattern is associated with a significant difference in altitude from the river bank to interstream spur (up to 100 m). Such abrupt relief restricts the zone of atmospheric pollution of soils are limited by this surface. In the area of a large protrusion of a river valley within the urban area itself, the pollution zone of the NPP likely shifts north and northwest along the edge zone of the Tuzlov river valley. It is noteworthy that in the soils from the most remote site (site 10), the concentrations of Pb_{tot} (18.0 mg/kg), Ni_{exc} (6.5 mg/kg) and Pb_{exc} (2.7 mg/kg) are increased. This situation is probably related to the presence of secondary sources of pollution such as vehicle emissions from the major highway that passes by the plant (Fig. 2).

Table 5 Statistical summary of PTEs concentrations (mg/kg, except for CV in %) in soils of the NPP impact area

Metal	n	Total concentration							Exchangeable fraction concentration						
		Mean	Median	Min	Max	SD	CV	SE	Mean	Median	Min	Max	SD	CV	SE
Cr	12	115.4	115.2	84.0	154.0	20.7	18.0	6.0	5.8	4.4	2.2	13.9	4.0	69.8	1.2
Mn	12	827.0	825.9	598.0	1044.1	165.3	20.0	47.7	56.1	37.7	20.1	141.0	43.0	76.7	12.4
Ni	12	58.4	56.9	31.0	91.0	18.7	32.0	5.4	3.2	2.7	0.5	7.4	2.1	67.0	0.6
Cu	12	53.0	54.3	30.0	80.0	14.0	26.5	4.1	3.4	3.7	0.4	6.7	1.7	51.1	0.5
Zn	12	108.7	112.0	70.1	155.0	24.1	22.2	7.0	9.9	8.1	1.8	27.9	8.0	81.2	2.3
Cd	12	0.80	0.60	0.35	1.85	0.49	61.3	0.14	0.09	0.05	0.01	0.35	0.10	114.3	0.03
Pb	12	41.9	38.0	18.0	73.0	16.8	40.1	4.8	4.9	3.7	1.3	9.4	2.8	56.5	0.8

n number of soil samples, *Min* minimum, *Max* maximum, *SD* standard deviation, *CV* coefficient of variance, *SE* standard error
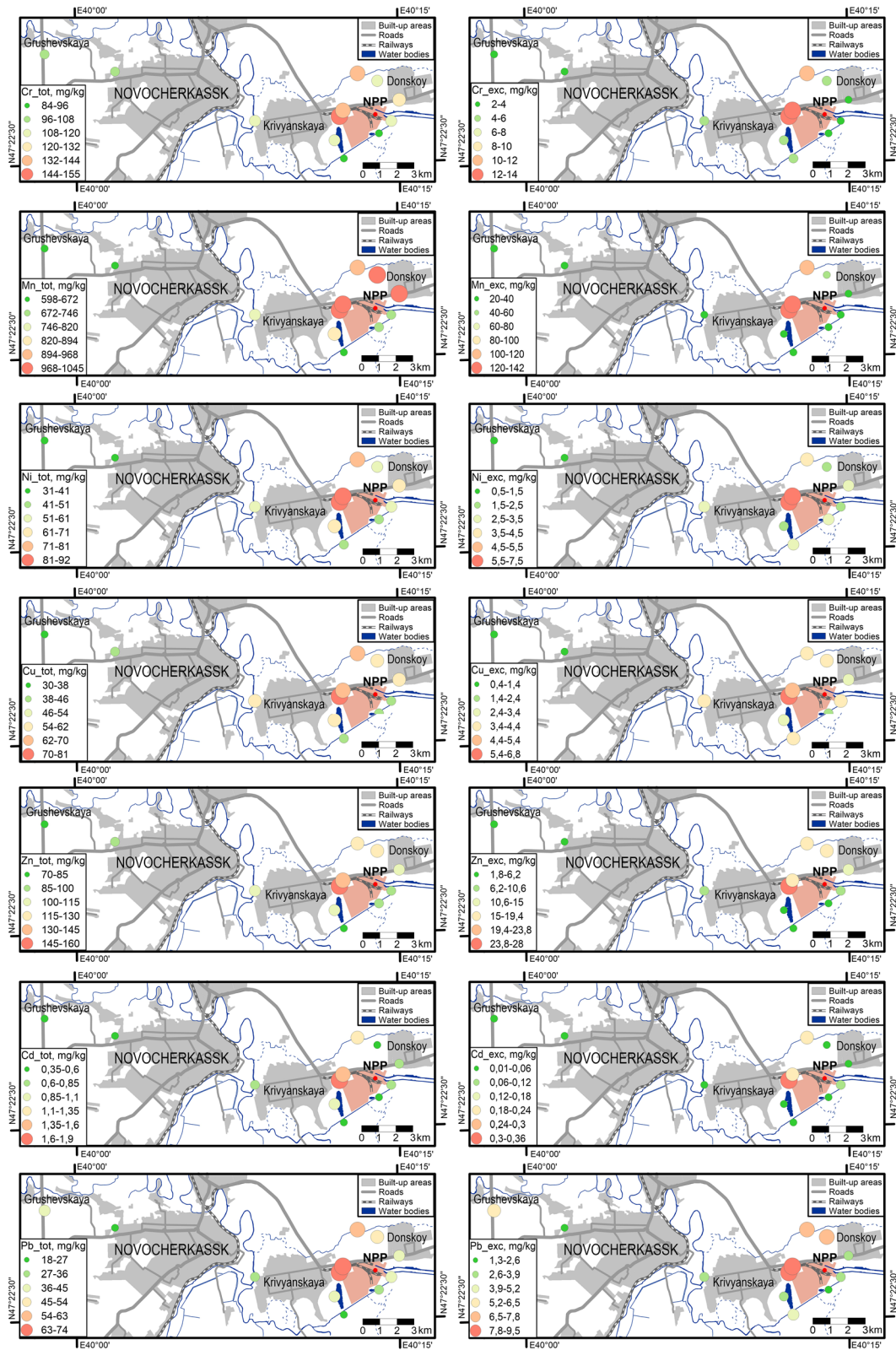
Thus, the impact zone of NPP is manifest to a distance of about 7 km, and the local circulation of air masses influences the spatial distribution of pollutants in soils with PTEs, while soil characteristics play a secondary role.

Ecological risk assessment

The soils in the study area are characterized by near-Clarke concentrations of Cr, Mn, Ni, Cu, Zn, and Cd (Fig. 3), while the total Pb content is on average 2.5 times higher than UCC (Table 2), reaching a maximum (3.5–4.3) in soils near the leeward zone of the NPP, which indicates a strong aerotechnogenic supply of this element. Site 4 soil had the largest excesses of Cu, Zn, and Cd (CC 2.1, 2.1, and 2.9, respectively). The average content of PTEs in soils within the impact area exceeded the world average (Table 2) by 1.4–2.0 (Fig. 3). The CC values are especially strong for Cr (1.4–2.6), Ni (1.1–3.1), Cd (0.9–4.5), and Pb (0.9–2.7), which indicates a significant accumulation of PTEs in the soils of the study area.

Analysis of I_{geo} showed that the soils in the near leeward zone of the NPP (Fig. 4) are most polluted at a distance of up to 3 km with moderate to high (site 4) and moderate (sites 5 and 6) pollution for Cd (I_{geo} 2.0, 1.8, and 1.5, respectively) and Pb (I_{geo} 1.1, 0.8, and 1.0, respectively). In terms of Cr, Ni, Cu, and Zn, according to the calculated I_{geo} values, the soils of these sites are unpolluted to moderately polluted. Soils near the windward zone are slightly contaminated with Zn, Cd, and Pb, which, according to I_{geo} values, correspond to class 1. A similar situation is typical for distant soils in the leeward zone.

A contrasting assessment of soil pollution with respect to the RB (Table 2) is provided by the PI (Fig. 5). Minimum PI values for all PTEs, except for Cd, were observed soils at site 2 (PI < 1.0), which indicate the absence of soil contamination by these elements. In general, soils in the impact area are not contaminated or lightly contaminated with Cr, Mn, Ni, Cu, and Zn, except for site 4 where the soil is moderately contaminated with Ni and Zn (PI 2.1 and 2.2, respectively). Moderate pollution by Cd (PI 2.0, site 1) and Pb (PI 2.3, site 7) was observed for the soils in the windward zone. Soils in the leeward zone to the west and northwest of the NPP (sites 4–6) were the most polluted with Cd and Pb, especially the soils at site 4 which show strong Cd and strong Pb contamination (PI 6.2 and 3.3, respectively). Estimates of soil pollution by PTEs using I_{geo} and PI are close; however, the PI allowed us to obtain a more detailed distribution of soils according to pollution classes (Fig. 5), while the degree of soil pollution by I_{geo} may be underestimated (Fig. 4).

A comprehensive assessment of soil pollution based on calculated NPI values indicates slight pollution of soils within the far leeward zone (1.3–1.7) and within the windward zone (1.2–1.9). In soils of the leeward zone, the degree of pollution, according to NPI values, decreases with distance, from heavy pollution near the source at sites 4–6 (3.3–4.8), moderate pollution at site 3 (2.3), and slight pollution at site 2 (1.3).

The ID was calculated for both total (ID_{tot}) and exchangeable forms (ID_{exc}) of PTEs (Fig. 6). No excess of permissible levels of ID_{tot} for Mn_{tot}, Cd_{tot}, and Pb_{tot} was observed in the impact area. The maximum ID_{tot} for Ni_{tot} (2.1), which corresponds to strong pollution, and that for Cu_{tot} (1.2) and Zn_{tot} (1.3), which corresponds to average pollution, were observed in soils at site 2 due to the application of more stringent standards in the assessment of sandy soils (Table 2). In general, soils of the NPP impact area were moderately contaminated with Cr_{tot} (ID_{tot} 1.3–1.9), while strong pollution was characteristic of soils representing the leeward zone (ID_{tot} 2.1–2.4, sites 4–6). Moderate pollution for Ni_{tot} (IDt_{ot} 1.1) was also
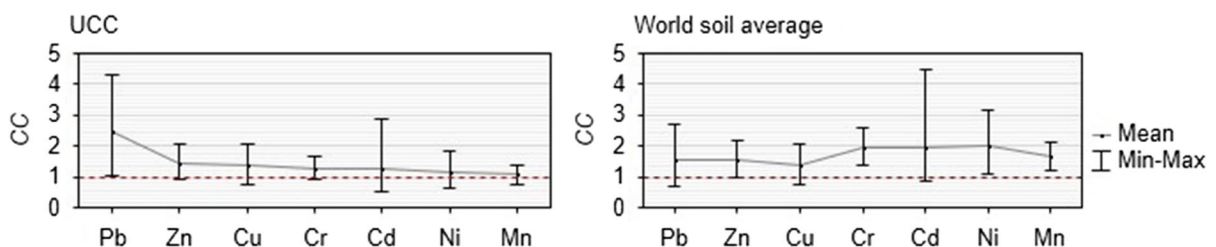

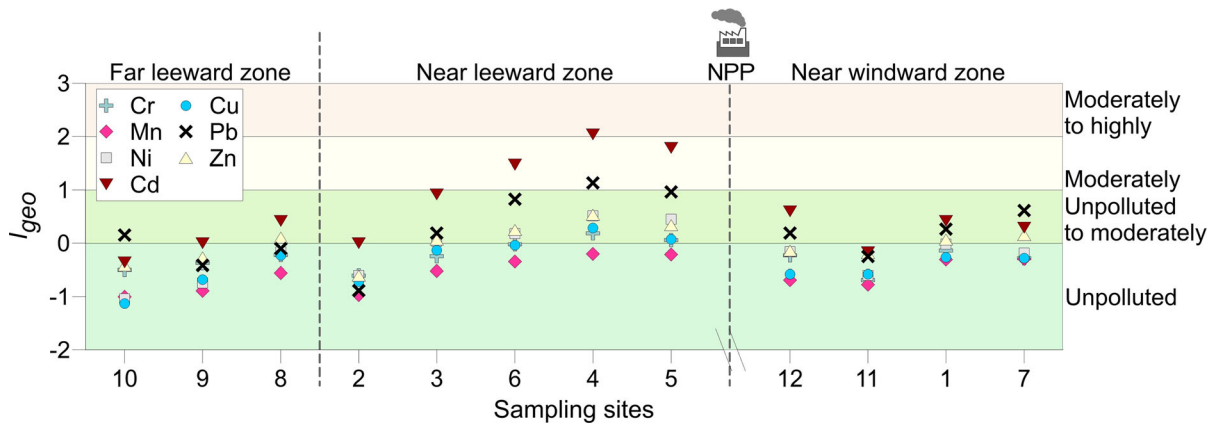Fig. 3 Concentration coefficient (CC) of PTEs in soils of the NPP impact area

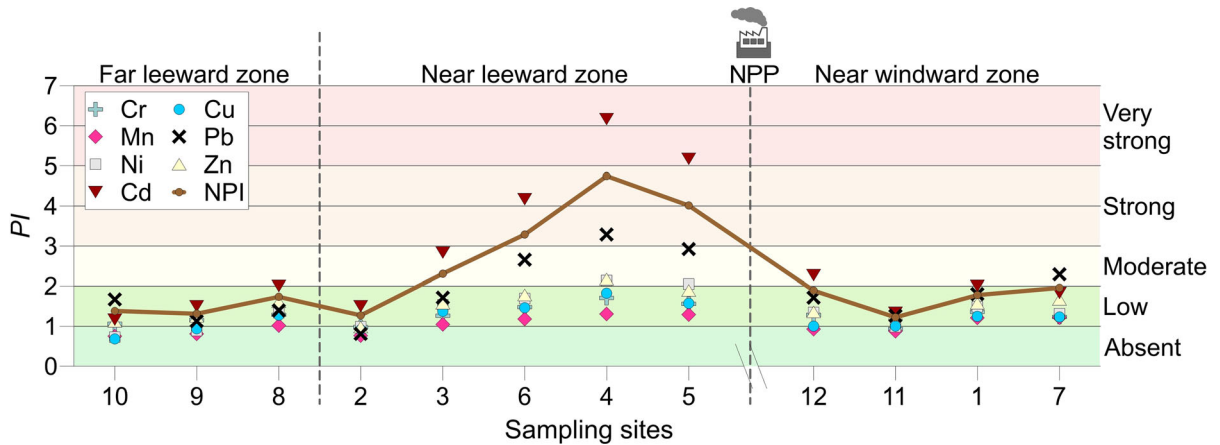**Fig. 4** Geoaccumulation index (I_{geo}) of PTEs in soils of the NPP impact area

Fig. 5 Single pollution index (PI) and Nemerow pollution index (NPI) of PTEs in soils of the NPP impact area

observed for these soils. A comprehensive assessment of pollution by SPI_{tot} showed that only soils at sites 2 and 4 were polluted, soils at sites 5 and 6 were problematic, and the rest were clean.

The assessment of soil contamination by exchangeable forms of PTEs using the ID_{exc} gives a slightly different picture (Fig. 6) compared to ID_{tot}, but is more consistent with the estimates obtained by I_{geo} (Fig. 4) and PI (Fig. 5). In general, the soils studied are characterized by low ID_{exc} values for Mn_{exc} and Zn_{exc} (0.2–0.9 and 0.1–0.8), while exceeding of the standards was noted at site 4 (1.0 and 1.2), which corresponds to moderate pollution. Moderate Ni_{exc} pollution (ID_{exc} 1.7–1.9) and strong Cr_{exc} pollution (ID_{exc} 2.0–2.3) appeared only in soils from the leeward zone, while moderate Pb_{exc} pollution (ID_{exc} 1.1–1.6) appeared in soils remote from the power plant, which

may be indicative of additional sources. Copper contamination in soil decreased with distance from NPP from strong contamination in soils at site 4 (ID_{exc} 2.2), to moderate contamination in soils near NPP (ID_{exc} 1.1–1.7), and low to absent at a considerable distance from the plant. According to calculated values of SPI_{exc}, only soils to the west and northwest of the NPP in the near leeward zone were polluted (1.1–1.7).

Human health risk assessment

Statistical data on the ADD for children and adults and the LADD are presented in Table 6. The highest doses of PTEs potentially enter the body through ingestion and the smallest dose through inhalation. No matter how the values of ADD and LADD of PTEs are
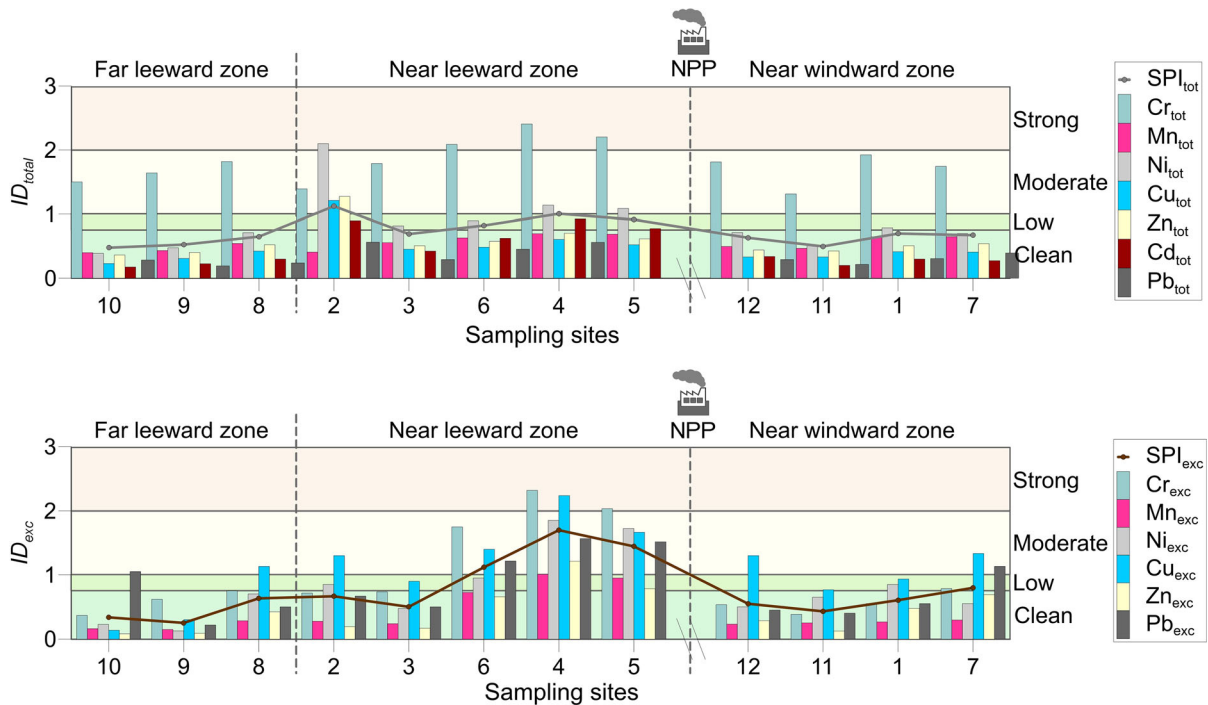
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Fig. 6 Index of danger (ID) and complex soil pollution index (SPI), characterizing the pollution level by the total content (ID_{tot}) and exchangeable fraction (ID_{exc}) of PTEs in soils from the NPP impact area

Table 6 Average health risk exposure (mg/kg/day) to noncarcinogenic hazards (ADD) for adults and children and carcinogenic hazards over a lifetime (LADD) attributed to the PTEs from soils in the NPP impact area

Receptor	Pathway	Dose	Cr	Mn	Ni	Cu	Zn	Cd	Pb	Total
Children	Ingestion	ADD_{ing}	1.5E−03	1.1E−02	7.5E−04	6.8E−04	1.4E−03	1.0E−05	5.4E−04	1.5E−02
	Dermal	ADD_{derm}	7.0E−05	2.5E−04	3.5E−05	1.6E−05	3.3E−05	2.4E−08	4.3E−05	4.5E−04
	Inhalation	ADD_{inh}	4.5E−08	3.2E−07	2.3E−08	2.1E−08	4.3E−08	3.1E−10	1.6E−08	4.7E−07
	Total	ADD_{total}	1.5E−03	1.1E−02	7.8E−04	6.9E−04	1.4E−03	1.0E−05	5.8E−04	1.6E−02
Adults	Ingestion	ADD_{ing}	1.4E−04	9.9E−04	7.0E−05	6.4E−05	1.3E−04	9.6E−07	5.0E−05	1.4E−03
	Dermal	ADD_{derm}	1.2E−05	4.2E−05	5.9E−06	2.7E−06	5.5E−06	4.0E−09	7.2E−06	7.5E−05
	Inhalation	ADD_{inh}	1.6E−08	1.2E−07	8.3E−09	7.5E−09	1.5E−08	1.1E−10	5.9E−09	1.7E−07
	Total	ADD_{total}	1.5E−04	1.0E−03	7.6E−05	6.6E−05	1.4E−04	9.6E−07	5.7E−05	1.5E−03
Lifetime	Ingestion	$LADD_{ing}$	1.7E−04	1.2E−03	8.4E−05	7.6E−05	1.6E−04	1.1E−06	6.0E−05	1.7E−03
	Dermal	$LADD_{derm}$	9.3E−06	3.3E−05	4.7E−06	2.1E−06	4.4E−06	3.2E−09	5.8E−06	6.0E−05
	Inhalation	$LADD_{inh}$	8.5E−09	6.1E−08	4.3E−09	3.9E−09	8.1E−09	5.9E−11	3.1E−09	8.9E−08
	Total	$LADD_{total}$	1.8E−04	1.2E−03	8.9E−05	7.8E−05	1.6E−04	1.2E−06	6.6E−05	1.8E−03

arrived at, they are proportional to their content in the soil.

To evaluate noncarcinogenic risks, the ADD values obtained in this study were compared with RfD. General toxic risks are more likely caused by intake of Pb, Ni, and Mn than all other PTEs (Fig. 7). For both

children and adults, the risk associated with the intake of PTEs was the greatest via ingestion (HQ_{ing} 0.38 and 0.04, respectively), slightly less through skin contact (HQ_{derm} 0.18 and 0.03, respectively), and insignificant via inhalation ($HQ_{inh} < 0.01$). The noncarcinogenic risk of exposure to individual and total PTEs is
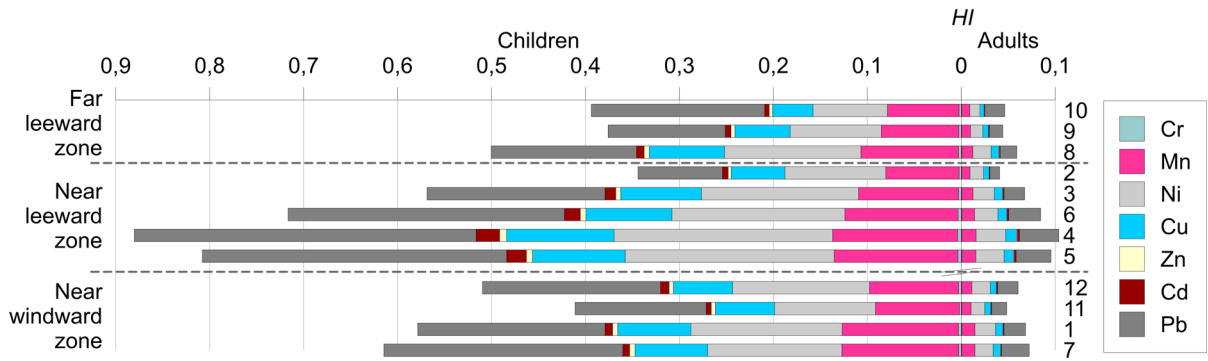
Fig. 7 Hazard Index (HI) via all pathways of exposure for adults and children based on total content of PTEs in soils from the NPP impact area

Table 7 Average and maximum lifetime cancer risk (CR) by individual PTEs through different exposure pathways and total cancer risk (TCR) from soils of the NPP impact area

Metal	CR_{ing}	CR_{derm}	CR_{inh}	TCR
Ni			3.6E−09/5.7E−09	3.6E−09/5.7E−09
Cd			3.7E−10/8.6E−10	3.7E−10/8.6E−10
Pb	5.1E−07/8.9E−07	2.5E−07/4.3E−07	1.3E−10/2.3E−10	7.6E−07/1.3E−06
Total	5.1E−07/8.9E−07	2.5E−07/4.3E−07	4.1E−09/6.8E−09	7.6E−07/1.3E−06

Mean and *maximum* values on either side of slash. Subscripts indicate the entry pathways of elements: *ing* ingestion, *derm* dermal contact, *inh* inhalation

assessed as negligible (HQ and HI less than 0.1) for adults. For children, the risk of general toxic effects caused by Mn, Ni, and Pb is, on average, low (average HQ 0.11, 0.15, and 0.21, respectively), while other PTEs do not appear to pose significant risk. The total noncarcinogenic risk was assessed as low in all samples (Fig. 7). The HI reached maximum values of 0.72–0.88 in soils in the near leeward zone.

Among the metals studied, only Ni, Cd, and Pb cause carcinogenic effects (Table 3). The assessment of carcinogenic risk showed that CR, regardless of the means of intake, corresponds to a negligible daily level. However, the cumulative TCR exceeds the threshold value of 1×10^{-6} in soils of the closest to the facility sites 4 and 5 (Table 7), which indicates the need for further monitoring of soils in this zone.

Conclusion

The results obtained in this study demonstrate the relationship between the features of atmospheric circulation and content of Cr, Mn, Ni, Cu, Zn, Cd, and Pb in soils of monitoring sites within the NPP impact zone. The highest values for both total and exchangeable forms of PTEs in soils were found over a radius of 1–3 km to the west and northwest of the NPP. This pattern is in good agreement with the prevailing wind directions. In addition to atmospheric emissions, dusting from the surface of ash dumps is a source of soil contamination by PTEs in the vicinity of the plant. However, identification and assessment of the contribution of this source requires additional study. The main pattern in spatial distribution of soil pollution within the area affected by NPP is a decrease in the concentrations of PTEs with distance from the source. The influence of NPP can be traced out to approximately 7 km downwind of the prevailing winds.

The total concentrations of Cr, Mn, Ni, Cu, Zn, Cd, and Pb in the soils around the NPP slightly exceed the Clarke values for the UCC, as well as the world average concentrations of these elements in soils (up to two times). An exception to this are the soils of the leeward zone of the power plant, which are characterized by significant accumulation of all PTEs except Mn. Moderate to high and moderate pollution by Cd

and Pb, according to the I_{geo}, is characteristic of the soils at a distance of up to 3 km to the west and northwest of the NPP. The PI also demonstrates higher pollution estimates relative to distance from the source; soils near the windward zone and outside a radius of 2 km in a westerly direction are characterized by low or no pollution by Cr, Mn, Ni, Cu, and Zn, and moderate pollution by Cd and Pb. Soils of monitoring sites located in the leeward zone (up to 3 km in the northwest and west directions) are moderately polluted with Ni and Zn and very strongly to strongly polluted with Cd and Pb. According to the comprehensive indicator NPI values, pollution decreases from heavy in the area immediately downwind of the source to slight for most of the territory under consideration.

Data of the sanitary-hygienic assessment of the total content of PTEs are somewhat at variance with the results of the pollution assessment derived from geochemical indicators. Thus, Cr is the main soil polluting agent, strongly polluting soils in the near-leeward zone and moderately polluting in soils elsewhere. The maximum contamination by Ni (strong) and Cu and Zn (moderate) was observed in *Calcaric Fluvic Arenosol* which presented relatively low levels of these elements, indicative of stringent environmental standards. At the same time, the level of soil contamination estimated ID calculated for exchangeable forms of PTEs was consistent with I_{geo} and PI values obtained. In general, the strongest pollution, by individual and complex PTEs, is manifest in the soils of the near leeward zone (moderate Mn, Ni, Zn, Pd pollution and strong Cr and Cu pollution), gradually decreasing with distance from NPP.

The risks of noncarcinogenic effects on children are assessed as low (HI 0.34–0.88), their occurrence is attributed to the intake of Mn, Ni, and Pb, while for adults there was no significant general toxic risk associated with the intake. Careful monitoring of the content of carcinogenic metals such as Ni, Cd, and Pb in soils is necessary because the TCR reaches target values in soils nearest the NPP impact zone.

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