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RESEARCH PAPER

## Impact of the Mednogorsk copper smelter on human health and soil environmental quality in the Orenburg Region, Russia

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### Abstract

**D. G. Polyakov, A. P. Zhikharev, M. M. Karpukhin, C. Yáñez, and A. Neaman. 2024. Impact of the Mednogorsk copper smelter on human health and soil environmental quality in the Orenburg Region, Russia. Int. J. Agric. Nat. Resour. 27-43.** Nonferrous metal smelting operations are a recognized source of metal accumulation in surrounding soils. In Mednogorsk, Russia, soil contamination results from atmospheric emissions from a local copper (Cu) smelter. This study aimed to assess health risks by analyzing the levels of Cu, arsenic (As), cadmium (Cd), lead (Pb), and zinc (Zn) in 20 Mednogorsk topsoil samples and three background area samples. The phytotoxicity of metals to *Lolium perenne* was also evaluated. The soil ingestion protocol of the US Environmental Protection Agency was used for health risk assessment. Phytotoxicity tests were performed on ryegrass using a standard protocol. The levels of Cu correlated with those of other elements, indicating that the smelter was the source. Of concern, the carcinogenic risk exceeded the  $10^{-04}$  threshold in 85% and 15% of the samples for children under five years of age and adults, respectively. In addition, 60% of the samples exceeded the safe Pb threshold for children's health (80 mg kg<sup>-1</sup>). These risk levels are unacceptable and require specific intervention by the relevant authorities. However, only 20% of the samples showed high phytotoxicity, mostly in acidic soils (pH<4.0). This discussion focuses on the potential of soil phytostabilization to reduce human metal exposure, as the results provide valuable insights for managing metal pollution in regions affected by nonferrous smelter emissions worldwide.

**Keywords:** hazard quotient, human health, *Lolium perenne*, metals, metalloids, urban soils

## Introduction

Soil contamination with trace elements in mining regions is a well-documented global issue, as numerous international studies have highlighted (Plumlee & Morman, 2011). Soil metal<sup>1</sup> contamination poses a hidden threat to human health (Ding et al., 2018; Xie et al., 2017; Yousaf et al., 2016). Nonferrous metal smelting operations are recognized as significant sources contributing to metal accumulation in surrounding soils (Ettler, 2016). The areas adjacent to the Mednogorsk Cu smelter in Russia's Orenburg Region (Figure 1) are particularly concerning because they have received atmospheric deposition from the smelter for six decades between 1939 and 1999. However, reports on the chemical composition of emissions from the Mednogorsk Cu smelter are scarce, highlighting the relevance of this study.

Between 1992 and 1999, smelter technology was modernized, resulting in reduced emissions (Kofeinikov et al., 2001). Currently, significant efforts are underway to further mitigate smelter emissions as part of the Russian government's "Clean Air" project (Ministry of Natural Resources and Environment, 2024). However, a recent study by Zaitseva and May (2023) reported poor air quality in the city of Mednogorsk and a high risk of respiratory diseases. Similarly, the study by Kuzmina et al. (2017) classified the population of Mednogorsk as vulnerable.

Inadvertent soil ingestion, such as through hand-to-mouth contact, represents an important pathway for human exposure to trace element contamination (Mielke, 2016). While research suggests that most children ingest relatively small amounts of soil, approximately 10% may ingest approximately



**Figure 1.** Location of the study area around the Mednogorsk smelter and background sampling sites.

<sup>1</sup> For simplicity, the term "metal" includes arsenic, a metalloid.

200 mg of soil daily, and a small fraction ingest greater amounts (Calabrese et al., 1989). The US Environmental Protection Agency (US EPA, 2011) recommends using accidental soil ingestion rate estimates of 50 mg day<sup>-1</sup> for children and 20 mg day<sup>-1</sup> for adults in human health risk assessments. Crucially, accidental soil ingestion is recognized as a significant metal exposure pathway in areas affected by copper smelter operations (Berasaluce et al., 2019).

In recent years, considerable attention has been given to secondary sources of pollution (Luo et al., 2014), such as industrially contaminated areas, which contribute to air and water pollution if left unaddressed. However, environmental remediation programs for such areas have consistently suffered from inadequate funding on a global scale. To reduce uncertainty in soil remediation outcomes, these efforts should be based on the established risks to human health posed by contaminated soils.

Remarkably, to the best of our knowledge, no existing studies have examined trace element levels in the soils of the city of Mednogorsk. Similarly, we are unaware of any research that has examined the potential human health risks associated with trace elements in the soils of the city of Mednogorsk. Therefore, the primary objective of this study was to assess the human health risks associated with trace element exposure in the vicinity of the Mednogorsk Cu smelter.

In addition, we sought to explore a practical strategy for reducing human exposure to trace elements in contaminated soils. In some of the study areas, visual observations revealed degraded vegetation and exposed soil. Restoring vegetative cover on contaminated soils offers a cost-effective means of reducing human exposure to trace elements. Plants can immobilize metals through root uptake (Mench et al., 2000) and release organic matter that chelates metal ions in the rhizosphere (Meier et al., 2012). In addition, vegetation restoration can reduce soil erosion (Bienes et al., 2016), improve

air quality (Bienes et al., 2016), minimize metal leaching from soils (Tordoff et al., 2000), reduce human exposure to metal-laden dust (Bierkens et al., 2011), and enhance the aesthetic appeal of previously vegetation-free land (Ivanova et al., 2020). Metal phytotoxicity, however, can hinder plant growth in contaminated soils. To assess the feasibility of restoring vegetative cover, a secondary objective was to evaluate metal phytotoxicity in the soils of the Mednogorsk community. For this purpose, a laboratory phytotoxicity bioassay was carried out using *Lolium perenne* as a bioindicator species.

## Materials and Methods

### *Study area*

The study area included the city of Mednogorsk (Figure 1), with dimensions of 5.4 km in width and 11.3 km in length and a total area of 61 km<sup>2</sup>. The population of the city is approximately 25,000 people (source: 56.rosstat.gov.ru), and the total area of the city is 86 km<sup>2</sup> (source: mo-mednogorsk.orb.ru/activity/31403). Consequently, the population density is calculated to be 290 persons per km. For reference, control soil samples (3 in total) were collected from an area situated 14–23 km to the south–southeast of the smelter (Figure 1).

### *Soil sampling and analysis*

A total of 23 topsoil samples (0–15 cm depth), each weighing approximately 3 kg, were collected for this study (Figure 1). Soil sampling locations were chosen based on their accessibility. The geographical coordinates of the sampling sites are given in Supplementary Table 1. The collected soil samples were dried at 40 °C for 48 hours and then sieved through a 2 mm mesh. Total Cu, As, Cd, Ni, Pb, and Zn were determined by inductively coupled plasma optical emission spectroscopy (ICP–OES, Agilent 5110, Malaysia). Soil digestion was performed by microwave digestion (Milestone

Inc., USA) according to the protocol specified in the Russian Federal Register FR 1.31.2009.06787, using 0.25 g of soil, *aqua regia* (6 mL HCl, 2 mL HNO<sub>3</sub>), and hydrogen peroxide (2 mL H<sub>2</sub>O<sub>2</sub>). Standard reference materials (Krasnozem and Chernozem, supplied by Ecolan, Russia) were used throughout the analysis, and the experimental values of the target trace elements were within 100 ± 20% of the certified values.

For the measurement of exchangeable trace elements in soils, a 0.01 M KNO<sub>3</sub> solution was used at a soil/solution ratio of 1/2.5. This suspension was stirred for 60 minutes and then filtered through ash free filter paper. The same ICP–OES instrument was used to quantify trace elements.

The soil pH was measured using a 1 M KCl extract with a soil/solution ratio of 1/2.5. Soil electrical conductivity was determined in aqueous extracts with a soil/solution ratio of 1/5. The organic matter concentration was determined by the wet combustion method using potassium dichromate and sulfuric acid (Sadzawka et al., 2006). Pearson correlations between trace element

concentrations were calculated using InfoStat software, version 2020p.

#### *Noncarcinogenic human health risk assessment*

This study focused on soil ingestion as the primary exposure pathway (Berasaluze et al., 2019). Exposure pathways such as inhalation or dermal contact were not considered. To determine the chronic daily intake (CDI) of trace elements, the methodology outlined by the US EPA (2011) was used. Specifically, CDI values were calculated separately for adults (≤60 years of age) and children (≤5 years of age).

The US EPA guidelines advocate the use of the annual intake rate, which is then converted to a daily intake of the trace element by dividing it by the number of days in the exposure period. The specific equation used for this conversion is as follows:

$$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (\text{Equation 1})$$

**Table 1.** Input parameters for the human health risk assessment.

Variable	Index	Unit	Value	Observation	Source
Soil ingestion rate	IR	mg day <sup>-1</sup>	2 · 10 <sup>-5</sup>	Adults	US EPA (2011)
			5 · 10 <sup>-5</sup>	Children	
Frequency of exposure	EF	day year <sup>-1</sup>	365	-	US EPA (2002)
Exposure duration	ED	year	30	Adults	US EPA (2002)
			2.5	Children	
Average body weight	BW	kg	70	Adults	US EPA (1989)
			15	Children	
Average duration	AT	day	10950	Adults	US EPA (1989)
			913	Children	
Reference dose	RfD	mg kg <sup>-1</sup> day <sup>-1</sup>	3 · 10 <sup>-4</sup>	As	US EPA (2002)
			35 · 10 <sup>-4</sup>	Pb	
			0.001	Cd	
			0.04	Cu	
			0.3	Zn	
Cancer slope factor	SF	(mg/kg · day) <sup>-1</sup>	0.02	Ni	US EPA (2011)
			1.5	As	
			0.0085	Pb	

where CDI is the chronic daily intake of the trace element ( $\text{mg}$  of trace element  $\text{kg}^{-1}$  of body weight  $\text{day}^{-1}$ ); C is the concentration of a given trace element in soil ( $\text{mg kg}^{-1}$ ); IR is the soil ingestion rate ( $50 \text{ mg day}^{-1}$  for children and  $20 \text{ mg day}^{-1}$  for adults); EF is the exposure frequency ( $365 \text{ days year}^{-1}$ ); and BW is the average body weight of the exposed person ( $70 \text{ kg}$  for adults and  $15 \text{ kg}$  for children).

The exposure duration (ED) in Equation 1 represents the number of years an individual has lived in the study area. In this study, individuals were assumed to have lived in the study area for their entire lives, which represents a worst-case scenario for exposure assessment. In addition, ED and AT (average exposure time in days) are age-specific and were calculated as half of the maximum age within each age group (Neaman et al., 2024). For example, in the case of the  $\leq 5$  years age group, the exposure duration (ED) was set at 2.5 years, resulting in an exposure time (ET) of 913 days ( $2.5 \text{ years } 365 \text{ days year}^{-1}$ ). It should be noted that by using these units in Equation 1, the resulting chronic daily intake values are appropriately expressed in  $\text{mg kg}^{-1} \text{ day}^{-1}$ . The parameters used to estimate the human health risk are summarized in Table 1.

For each specific trace element, we used the oral reference dose (RfD) value shown in Table 1. To assess the potential health risk associated with each trace element, we calculated the hazard quotient (HQ) by dividing the derived chronic daily intake (CDI) values by the respective reference dose (RfD). This calculation was performed using the following equation:

$$HQ = \frac{CDI}{RfD} \quad (\text{Equation 2})$$

Hazard quotient values less than 1 are considered safe for the local population, while values equal to or greater than 1 are considered unsafe for human health, according to (US EPA, 2011) guidelines.

Notably, in some studies, such as Nkansah et al. (2017), hazard quotient values for individual trace elements were aggregated to calculate a hazard index. However, this approach is not consistent with the US EPA (1986) principles. This is because different trace elements can have different effects on human health (Adriano, 2001). Therefore, summing hazard quotients is inappropriate because these different trace elements do not have an additive effect on health.

#### *Cancer risk assessment*

Cancer risk was calculated as the increased probability of an individual developing cancer over a lifetime due to exposure to a potential carcinogen. To estimate this risk, we multiplied the chronic daily intake (CDI) value (expressed in  $\text{mg kg}^{-1} \text{ day}^{-1}$ ) by the corresponding slope factor ( $\text{mg/kg day}^{-1}$ ). This multiplication resulted in a unitless probability of risk (US EPA, 1995). Specifically, the following equation was used:

$$\text{Cancer risk} = CDI \times SF \quad (\text{Equation 3})$$

According to the guidelines established by the United States Environmental Protection Agency (US EPA, 2001), the threshold value for cancer risk is  $1.0 \cdot 10^{-4}$ . For instance, cancer risk values ranging from 1:1,000 to 1:10,000 are considered unacceptable, whereas cancer risk values ranging from 1:10,000 to 1:100,000 are considered acceptable. It is important to emphasize that among the elements studied in this study, slope factor values were available only for As and Pb, as shown in Table 1.

#### *Phytotoxicity assessment*

A plant bioassay was performed according to a standardized protocol (ISO 11269-2, 2012), as previously described in our publications (Dovletyarova et al., 2023; Tarasova et al., 2020). Perennial ryegrass (*Lolium perenne* L.) was chosen as

the bioindicator for this study due to its increased sensitivity to metal toxicity (Grigorita et al., 2020). Three replicates of ryegrass were grown on all soil types, including background soils.

Each growth experiment lasted 21 days and was conducted under controlled conditions in a growth chamber. The light cycle was 16 hours with a photosynthetically active radiation level of  $206 \pm 38 \mu\text{M m}^{-2} \text{s}^{-1}$ . Each pot contained 100 planted seeds, and the soils were regularly irrigated by surface spraying with distilled water every two days.

A multipurpose fertilizer (Fertika, Russia) was applied to all soil samples according to the manufacturer's recommendations for grass species at a rate of 0.4 g fertilizer per 1 kg substrate. The fertilizer components included  $\text{NH}_4\text{-N}$  (6.6%),  $\text{NO}_3\text{-N}$  (4.4%),  $\text{P}_2\text{O}_5$  (12%),  $\text{K}_2\text{O}$  (26%),  $\text{MgO}$  (0.4%),  $\text{S}$  (0.7%),  $\text{Ca}$  (0.55%),  $\text{Mn}$  (0.16%),  $\text{Cu}$  (0.08%),  $\text{B}$  (0.09%),  $\text{Fe}$  (0.16%),  $\text{Zn}$  (0.09%), and  $\text{Mo}$  (0.008%). Therefore, nutrient deficiencies did not limit plant growth, especially considering that ryegrass has low nutrient requirements during its early growth stages (Verdejo et al., 2015).

At the end of the 21-day experiment, the plants were harvested by cutting. To prepare them for analysis, a thorough washing process was used, which included sequential rinses with tap water, distilled water, and a final rinse with distilled water. The plants were then dried in an oven set at  $70^\circ\text{C}$  for 48 hours to determine their shoot dry weight.

Measurement of foliar elemental concentration was performed using ICP–OES following a standard procedure of dry ashing at  $600^\circ\text{C}$  and element extraction from the ash using 2 M  $\text{HCl}$  (Sadzawka et al., 2007). In a number of cases, plant growth in certain soils was severely impaired, resulting in insufficient biomass for analysis. To maintain consistency of analysis across all samples, leaf analysis was performed in all cases using composite samples obtained from three replicates (Supplementary Table 3). Standard reference

materials from the Pryanishnikov All-Russian Scientific Research Institute of Agrochemistry were used throughout, and experimental values for the target trace elements were within  $100 \pm 20\%$  of the certified values. The plant responses are summarized in Supplementary Table 3.

For each sampling point, we determined the pollution index according to the method described by Vorobeichik and Pozolotina (2003) using the following formula:

$$PI_i = \frac{1}{n} \sum_{j=1}^n \left( \frac{C_{ji}}{C_{jb}} \right) \quad (\text{Equation 4})$$

where  $PI_i$  is the pollution index of the  $i$ th point,  $C_{ji}$  is the exchangeable concentration of the  $j$ th element at the  $i$ th point,  $C_{jb}$  is the average concentration of the  $j$ th element in the background samples, and  $n$  is the number of elements analyzed. The contamination index represents the average increase in contamination of all trace elements compared to background levels.

It is widely recognized that the total concentration of trace elements in soils is not sufficient to predict their potential phytotoxicity (Adriano, 2001). Typically, chemically nonaggressive neutral salts are used to extract the exchangeable fractions of trace elements, which are considered more informative for assessing metal phytotoxicity in contaminated soils (Lillo-Robles et al., 2020; McBride et al., 2009). In our study, we calculated the contamination index (Equation 4) based on exchangeable metal concentrations to address this consideration. Specifically, in our study, the contamination index was determined based on the exchangeable concentrations of  $\text{Cu}$ ,  $\text{Ni}$ , and  $\text{Zn}$  (i.e.,  $n=3$  in Equation 4). This choice was made because the exchangeable concentrations of other trace elements in the background soils were below the detection limits, making them unsuitable for inclusion in the calculations.

We then plotted shoot dry weight against the soil contamination index. The 25% effective concen-

tration ( $EC_{25}$ ) was estimated using the Toxicity Relationship Analysis Program (TRAP), version 1.30a (US EPA, 2016). The pollution index served as the dose variable, while shoot dry weight was the response variable. For the reference value (set at 100%), we used the average shoot dry weight of plants grown in the background soils. In addition, we plotted shoot dry weight against the foliar (i.e., ryegrass shoot) concentration of each trace element.

### *Visual presentation of the results*

To enhance visual understanding of the results obtained, plots were generated using Surfer® software version 13.3.493 from Golden Software in Colorado, USA. The analysis employed the kriging procedure provided by the software, utilizing the linear variogram model with default values of 1 for both slope and anisotropy.

## **Results and Discussion**

### *Concentrations of trace elements in the study area*

In the study area, strong and positive correlations were observed between total soil Cu and total soil As ( $r=0.86$ ), Cd ( $r=0.99$ ), Pb ( $r=0.96$ ), and Zn ( $r=0.99$ ), with all correlations showing high statistical significance ( $p<0.0001$ ). The strong correlations among these trace elements suggest a common contamination source, likely the Cu smelter. Notably, As, Cd, Cu, Pb, and Zn are chalcophile elements known for their strong affinity for sulfur (Goldschmidt, 1937). Consequently, their simultaneous presence in Cu ores is expected and has been documented in previous studies worldwide (Tapia-Gatica et al., 2020; Tepanosyan et al., 2020; Zhikharev et al., 2022). In contrast, the total soil Cu concentration showed no correlation with that of Co or Ni. These two elements belong to the siderophile group, which is characterized by its affinity for iron (Alloway, 1995). Therefore, their occurrence in Cu ores is

less likely, which explains the lack of correlation with the Cu concentration.

The natural concentrations of total Cu, As, Cd, Pb, and Zn in the investigated soils were  $43\pm 15$ ,  $16\pm 6$ ,  $0.87\pm 0.81$ ,  $29\pm 25$ , and  $96\pm 39$  mg kg<sup>-1</sup>, respectively (see Supplementary Table 1). These results are in close agreement with those reported by Dovletyarova et al. (2023) for an area 56 km north–northwest of Orenburg, who reported values of 12, 0.43, 75, 12, and 59 mg kg<sup>-1</sup>, respectively, for the same elements. This consistency underscores the generalizability of our research results.

The concentrations of As, Cd, Cu, and Pb in the studied soils are graphically presented in Figure 2. Notably, in areas adjacent to smelters, trace element concentrations in soils typically show spatial trends influenced by prevailing wind directions (González et al., 2014). However, in our study area, there was no predominant wind direction; rather, the wind direction was highly variable (source: world-weather.ru/archive/russia/mednogorsk). Our study was conducted in a relatively small area, which limits our ability to detect spatial trends in the distribution of soil trace element concentrations around the Mednogorsk Cu smelter. Future investigations should include broader spatial coverage to provide a more comprehensive understanding of this phenomenon.

### *Evaluation of human health effects of trace elements in the area under study*

Arsenic has emerged as the element of greatest concern in terms of human health risk. In adults, As was the sole contributor to human health risk (see Supplementary Table 4). The noncarcinogenic risk levels for adults were generally low, with hazard quotient values exceeding 1.0 in only 10% of the samples investigated (see Figure 3A). Similarly, the carcinogenic risk to the adult population exceeded the threshold of  $10^{-04}$  in only 15% of the samples (see Figure 3C).

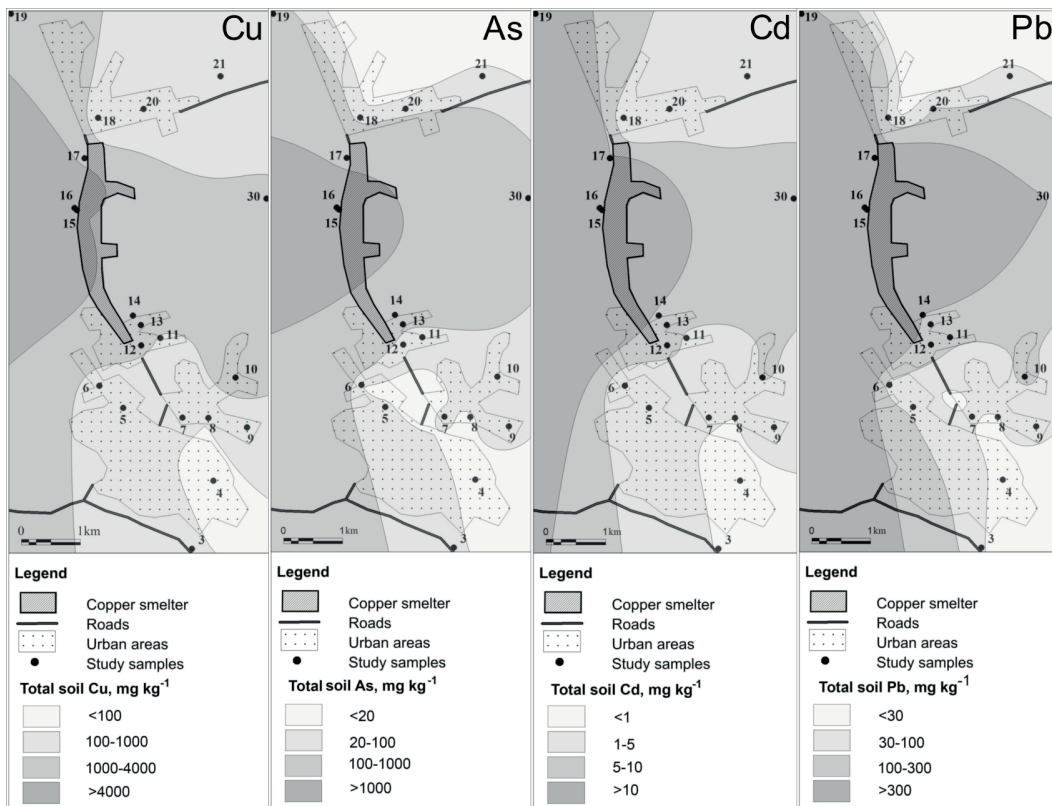


Figure 2. Spatial distribution of total concentrations of total Cu, As, Cd, and Pb in topsoil in the study area.

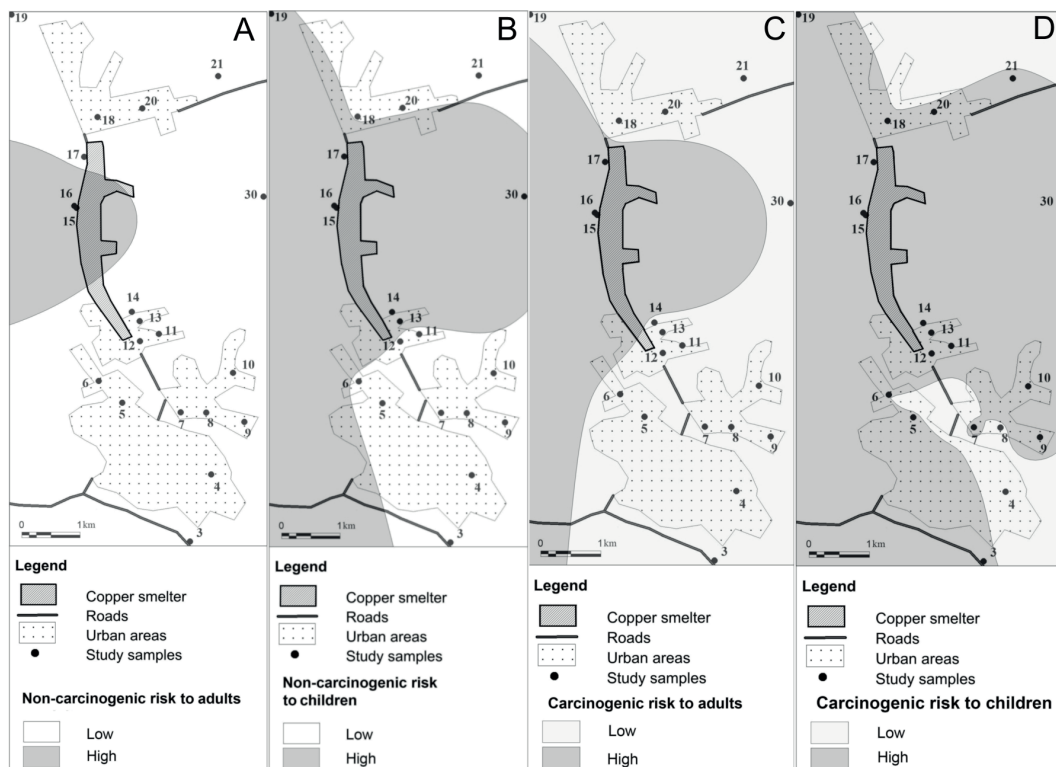
However, the noncarcinogenic risk associated with As for young children ( $\leq 5$  years) was significantly greater, with hazard quotient values exceeding 1.0 in 35% of the samples (Figure 3B). Of greater concern, the cancer risk for the child population exceeded the  $10^{-04}$  threshold in 85% of the samples (see Figure 3D). These cancer risk levels are considered unacceptable by the US EPA (2001) and require specific intervention by the relevant authorities.

It is worth noting that the acceptable daily intake of As for children is typically not exceeded even at relatively high soil intakes of  $20 \text{ mg kg}^{-1}$  As (Mielke et al., 2011). However, in this study, the vast majority of the soil samples (17 out of 20, or 85%) surpassed this threshold. It should be noted that the exposure assessment assumed that individuals lived in the study area for their entire lives, representing a worst-case scenario. Therefore, future studies incorporating more

nuanced exposure scenarios are required for comprehensive human risk assessments.

For Pb exposure in children, both noncarcinogenic and carcinogenic risks were relatively low, occurring in only 10% of the samples. However, it is important to note that existing research has documented a positive nonlinear relationship between soil Pb concentrations and blood Pb concentrations in children in the USA (Laidlaw et al., 2005; Mielke et al., 2007; Zahran et al., 2011). Specifically, children showed a significant increase in blood Pb concentration when soil Pb levels exceeded  $100 \text{ mg kg}^{-1}$  (Mielke et al., 1999). These findings support a safer soil Pb concentration of  $80 \text{ mg kg}^{-1}$  for most children (Mielke et al., 1999). In the soils examined in our study, 12 out of 20 samples (i.e., 60%) exceeded this threshold and warranted specific intervention by the relevant authorities.





**Figure 3.** Noncarcinogenic risks from As to adults (A) and children aged  $\leq 5$  years (B). Carcinogenic risks from As for adults (C) and children aged  $\leq 5$  years (D). The threshold criteria are detailed in the text and Supplementary Table 4.

In contrast, Cu toxicity is generally not a concern for human health due to the presence of homeostatic mechanisms that control its excretion (Turnlund et al., 2005). Similarly, the risk of human exposure to Zn in the Mednogorsk community is negligible, as only one soil sample had a total Zn concentration exceeding the proposed human toxicity threshold of  $2200 \text{ mg kg}^{-1}$  for residential areas (Shayler et al., 2009). Furthermore, the noncarcinogenic risks associated with Cd in both adults and children were negligible (Supplementary Table 3).

#### *Phytotoxicity assessment*

To estimate the phytotoxicity, we relied on an experimentally derived dose–response curve (Supplementary Figure 1). In this context, Recatalá et al. (2012) suggested that soil quality standards should ideally fall between  $EC_{10}$  and  $EC_{50}$  (effective concentrations of 10% and

50%, respectively). However, 50% inhibition represents a significant effect (Stark et al., 2004), while  $EC_{10}$  values result in negligible or minimal effects, often falling within the “noise level” of the control response (Checkai et al., 2014). Therefore, in our study, we used the 25% effective concentration ( $EC_{25}$ ) value of the pollution index, which corresponds to 61 (Supplementary Figure 1). According to these  $EC_{25}$  values, 80% of the investigated samples exhibited low phytotoxicity, while only 20% exhibited high phytotoxicity (Figure 4A).

It is important to note that the region characterized by high phytotoxicity largely coincided with areas with acidic soils ( $\text{pH} < 4.0$ ) (Figure 4B). Under acidic soil conditions, metals tend to be more soluble (McBride, 1994), making them more readily available to plants. This increased phytoavailability may explain the reduced plant growth observed in acidic soils.

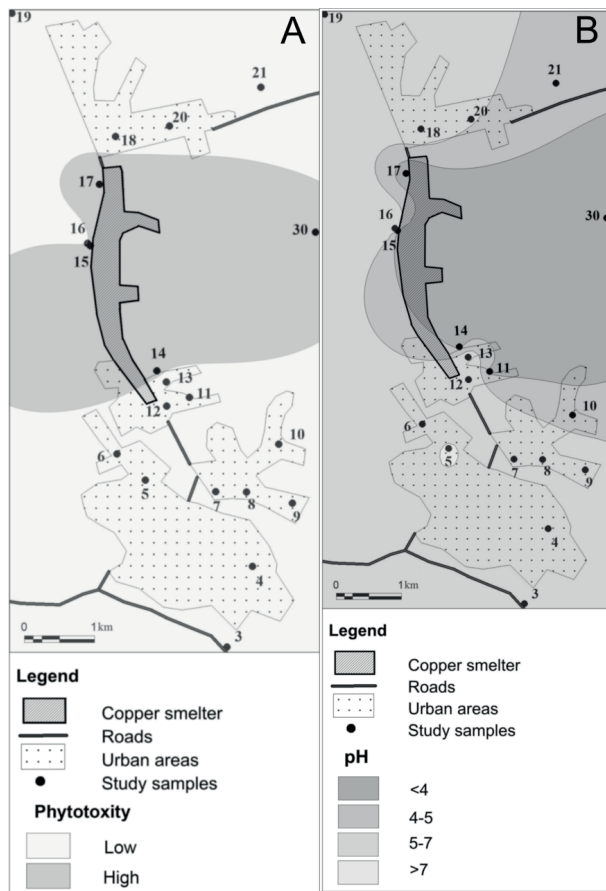


Figure 4. Spatial distribution of (A) potential phytotoxicity and (B) topsoil pH in the study area.

For the trace elements examined in our study, the foliar Cu concentration had the strongest correlation with the variance in ryegrass shoot dry weight (see Supplemental Figure 2). This suggests that Cu was the primary trace element responsible for phytotoxicity in the soils studied. However, due to the presence of multiple metallic contaminants, it is difficult to pinpoint the exact cause of phytotoxicity in these soils.

#### *Possible ways of remediating contaminated soils*

Regarding potential soil remediation methods in the Mednogorsk area, phytoextraction has been proposed as a cost-effective approach in numerous studies. However, phytoextraction is often impractical due to the long time required for remediation (Santa-Cruz et al., 2023). In contrast, the restora-

tion of vegetation cover on contaminated soils, known as phytostabilization, provides a relatively inexpensive and straightforward pathway to soil remediation (Mahar et al., 2016).

Restoring vegetative cover on contaminated soils may require the application of various organic and/or inorganic substances, hereafter referred to as amendments. The use of amendments, along with associated adsorption and/or precipitation reactions, can help reduce the bioavailability of metals in the soil. This process does not remove the metal from the soil but converts it to a less bioavailable form. As a result, metals become less accessible to plants and soil organisms (Ruttens et al., 2006). In addition, amendments can improve other soil properties that may hinder plant growth, such as nutrient deficiencies, low microbial activity, poor physical properties, etc. (Mench et al., 2000).

Lime and organic matter are two commonly used amendments for the remediation of chemically degraded soils (Quintela-Sabaris et al., 2017; Yan-Bing et al., 2017). Lime is effective at reducing the bioavailability of metals in contaminated acidic soils through the formation of new solid phases (such as metal precipitation or coprecipitation) or interactions with the surface of existing particles (such as metal adsorption) (Ma et al., 2006). On the other hand, organic amendments can provide essential nutrients such as nitrogen and phosphorus, improve soil water retention, and adsorb metals (Tordoff et al., 2000; USEPA, 2007).

Long-term studies in central Chile's semiarid climate have demonstrated that a single application of lime and organic matter is sufficient for sustainable revegetation of industrially contaminated sites. This suggests that repeated applications of the amendments may not be necessary (Pardo et al., 2018). Importantly, while Córdova et al. (2011) used irrigation in their phytostabilization trials in the same semiarid region, Ulriksen et al. (2012) showed that the phytostabilization process is feasible without irrigation. Under Mednogorsk's similar semiarid conditions, comparable results can be expected, suggesting that the restoration of vegetation cover on polluted and acidified soils is a viable option for the area.

#### *Future research needs*

This study identified As as the most significant health hazard in the soils of the Mednogorsk region. Understanding the pathways of human exposure to As is crucial for designing effective remediation and mitigation measures to protect the local population. One such exposure pathway is the ingestion of As through the food chain, particularly with regard to the presence of urban vegetable gardens in Mednogorsk. It is well known that As concentrations in vegetables can increase with increasing soil As levels (McBride, 2013).

Studies by Bacigalupo and Hale (2012) and Lizardi et al. (2020) have highlighted the importance of the vegetable consumption pathway for inorganic As exposure, which can rival the importance of accidental soil uptake. In addition, Neaman et al. (2024) emphasized that vegetable consumption in high-As soils may be an even more important pathway for inorganic As exposure than soil ingestion. Therefore, future research should be conducted to assess human exposure to As through vegetable consumption in the city of Mednogorsk and to comprehensively address this potential health risk.

Soil fauna, especially the earthworm *Eisenia fetida*, provide valuable information for the ecological assessment of soil quality. This bioindicator organism has been widely used to assess metal toxicity in contaminated soils (Neaman & Yáñez, 2023; Pelosi et al., 2021). Future studies using earthworms should aim to establish thresholds for exchangeable metal concentrations that induce toxicity in these organisms. In addition, the spatial distribution patterns of phytotoxicity risk identified in this study should be corroborated by examining field conditions, including observations of plant species richness and abundance, as demonstrated in other studies (Ginocchio, 2000; Vorobeichik et al., 2014).

It is important to note that potable water is an important pathway for human exposure to trace elements. In particular, a study by Korneeva et al. (2017) highlighted that acid drainage from mines near Mednogorsk affected the water quality of rivers and streams in the region. However, the quality of potable water in Mednogorsk remains unknown, and future research in this regard is needed.

#### **Conclusions**

This study represents the first comprehensive assessment of human health risks from trace element exposure in soils near the Mednogorsk Cu

smelter (Orenburg Region, Russia). Alarming, the carcinogenic risk for children aged  $\leq 5$  years exceeded the  $10^{-04}$  threshold in 85% of the samples studied. In addition, 60% of the samples exceeded the safe Pb threshold of  $80 \text{ mg kg}^{-1}$  for children's health. These risk levels are considered unacceptable and require specific intervention by authorities. In contrast, only 20% of the samples exhibited high phytotoxicity, mainly in areas with acidic soils ( $\text{pH} < 4.0$ ). Given these findings, restoring vegetation cover on polluted and acidified soils appears to be a viable option for the Mednogorsk area.

The identification of human exposure pathways to trace elements in contaminated areas is crucial for the implementation of tailored remediation and mitigation measures to protect local populations. Consequently, we believe that our findings provide valuable insights for addressing metal-related concerns in other regions of the world struggling with emissions from nonferrous smelters.

It is important to acknowledge the inherent limitations of this study in assessing human health risks associated with exposure to As and Pb in soils. This study was based on a relatively small dataset consisting of 20 topsoil samples from the urban area of the city of Mednogorsk and three

topsoil samples from an unpolluted background area. This limited sample size and spatial coverage underscore the need for future research efforts to include a wider range of samples and a larger geographic area.

Expanding the dataset to include a larger sample size and broader geographic coverage is essential to achieve a more comprehensive and robust understanding of the spatial distribution of the impacts of the Mednogorsk Cu smelter on human health and soil quality. Further research efforts should aim to address these limitations and provide a more complete assessment of the situation.

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#### Data availability

The data are available in Supplementary Material: <https://drive.google.com/uc?id=1wsOotZ3Ty-AURFBn4zsPCqLF1MVBBi dQy>

#### Resumen:

**D. G. Polyakov, A. P. Zhikharev, M. M. Karpukhin, C. Yáñez, y A. Neaman. 2024. Impacto de la fundición de cobre de Mednogorsk en la salud humana y la calidad del medio ambiente del suelo en la región de Orenburgo, Rusia. Int. J. Agric. Nat. Resour. 27-43.** Las fundiciones de metales no ferrosos son una fuente reconocida de acumulación de metales en los suelos circundantes. En Mednogorsk, Rusia, la contaminación del suelo se debe a las emisiones atmosféricas de una local fundición de cobre. Este estudio tiene como objetivo evaluar los riesgos para la salud humana mediante el análisis de los contenidos de cobre, arsénico, cadmio, plomo y zinc en 20 muestras de suelos de Mednogorsk y tres muestras de suelos del área no contaminada. Complementariamente, se evaluó la fitotoxicidad de los metales para una especie indicadora, *Lolium perenne*, utilizando un protocolo estándar. Para la evaluación de riesgos para la salud humana, se utilizó el protocolo de la Agencia de Protección Ambiental de los EEUU. Los contenidos de cobre se correlacionaron con los de otros elementos, lo que indica que la fundición de cobre es la fuente de emisión. Lo preocupante es que el riesgo cancerígeno superó el umbral de  $10^{-4}$  en el 85% de las muestras para niños de edad  $< 5$  años y en el 15% de las

muestras para los adultos. Además, el umbral de plomo considerado seguro para la salud infantil ( $80 \text{ mg kg}^{-1}$ ) se superó en el 60% de las muestras. Estos niveles de riesgo son inaceptables y requieren una intervención específica por parte de las autoridades pertinentes. Sin embargo, sólo el 20% de las muestras mostraron alta fitotoxicidad en *L. perenne*, principalmente en suelos ácidos (con  $\text{pH} < 4,0$ ). Considerando estos resultados, se evalúe la factibilidad de un proceso de fitoestabilización del suelo para reducir la exposición humana a los metales. Los resultados proporcionan información valiosa para gestionar la contaminación por metales en regiones afectadas por emisiones de fundiciones no ferrosas en todo el mundo.

**Palabras clave:** Cociente de riesgo, *Lolium perenne*, metales, metaloides, suelos urbanos, salud humana.

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