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Research Article

Spatial and temporal analysis of the distribution of copper in soils affected by the long-term impact of copper smelter—Aurubis Bulgaria AD

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Abstract

This study investigates the spatial and temporal distribution of copper (Cu) in soils affected by long-term atmospheric emissions from a major copper smelter in the Zlatitsa–Pirdop Valley, Bulgaria. The objective is to assess how industrial activity and subsequent technological changes influenced Cu accumulation patterns over a 48-year period (1973–2021).

Soil samples were collected along eastward transects at multiple distances from the smelter and analyzed using standard aqua regia digestion followed by atomic absorption spectrometry (AAS) and inductively coupled plasma optical emission spectrometry (ICP-OES) techniques. Three temporal datasets (1973, 1995 and 2021) were compared to evaluate long-term changes in Cu concentrations and spatial distribution.

The results show a pronounced shift in contamination patterns over time. In 1973, Cu concentrations exhibited a clear decrease with distance from the emission source, indicating localized deposition. In contrast, data from 1995 and 2021 reveal a more complex spatial pattern, with persistently elevated Cu levels at greater distances from the smelter. This change reflects modifications in emission release height, atmospheric dispersion conditions, and long-term redistribution processes.

The study demonstrates that Cu behaves as a persistent and poorly mobile contaminant in surface soils, with limited natural attenuation over decadal time scales. Despite significant improvements in emission control technologies after industrial privatization, historical deposition continues to dominate current soil contamination levels.

The findings highlight the combined role of anthropogenic emissions, valley topography, meteorological conditions, and local geochemical background in controlling heavy metal distribution. This study contributes to a better understanding of long-term soil contamination dynamics in industrial mountain-valley environments and provides a basis for environmental monitoring and risk assessment strategies.

Key words: Copper smelter, dynamics, humus horizon, soil pollution

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Introduction

Soils constitute a fundamental component of terrestrial ecosystems and are highly vulnerable to anthropogenic pressures. Consequently, changes in soil health may pose significant risks to ecosystem functioning. In particular, contamination by heavy metals represents a major environmental concern, as it may adversely affect soil quality, biodiversity, and human health. Within the European Union, soil contamination remains a critical environmental issue, with more than 2.5 million potentially contaminated sites and approximately 342,000 confirmed contaminated areas, according to Panagos et al. (2013).

A major source of copper (Cu) pollution in the environment is atmospheric emissions from non-ferrous metallurgical activities. A substantial fraction of Cu-bearing particulate matter is deposited on surrounding soils via wet and dry deposition, particularly where smelters are located in rural or peri-urban environments, according to Zhou et al. (2018). This atmospheric deposition results in the long-term accumulation of Cu in soils and crops, increasing exposure risks through food-chain uptake (Song et al. 2012; Fernández-Olmo et al. 2014; Khazaee et al. 2016; Vorobeichik and Kaigorodova 2017). Comparable long-term accumulation patterns have been documented globally, including in Luanshya, Zambia, where extremely elevated Cu concentrations were reported in surface soils near smelting facilities, according to Baieta et al. (2023).

According to Ragaini et al. (1977), Freedman and Hutchinson (1980), Løbersli and Steinnes (1988), Dumontet et al. (1992), McBride et al. (1997) and Barcan and Kovnatsky (1998), Ding et al. (2023), heavy metal contamination derived from smelter emissions is well documented. Atmospheric transport processes enable dispersal over distances ranging from a few kilometers to more than 100 km, according to Henderson et al. (1998), McMartin et al. (1999), García et al. (2004), and Martley et al. (2004). Therefore, understanding the mechanisms controlling spatial distribution is essential for developing effective environmental management and mitigation strategies (Shamsaddin et al. 2020). According to Aminiyan et al. (2022), potentially toxic elements remain strongly enriched in topsoils surrounding copper smelters, indicating the long-term persistence of anthropogenic inputs.

Given that copper is a non-biodegradable element, its accumulation in soils is long-lasting and requires long-term remediation strategies, according to Luo et al. (2005). According to Zabetoglou et al. (2003), Ballabio et al. (2018), heavy metals can be toxic even at low concentrations due to their tendency to accumulate in living organisms and the environment.

This study addresses the following research questions:

1. How have long-term atmospheric emissions from a copper smelter influenced the spatial distribution and temporal accumulation of Cu in soils of the eastern Zlatitsa–Pirdop Valley between 1973 and 2021?
2. To what extent do atmospheric emissions control Cu dispersal and long-term accumulation along the eastern transect of the valley?

The study aims to evaluate long-term Cu dynamics, the role of atmospheric transport, and the influence of local lithogeochemical background on contamination patterns. By integrating a 48-year dataset, the study provides a rare temporal perspective on technogenic soil contamination.

Materials and methods

Research problem and environmental context

The study tested the hypothesis that long-term atmospheric emissions from the copper smelter have significantly altered the spatial and temporal distribution of Cu in soils of the Zlatitsa–Pirdop Valley. Additional hypotheses evaluated the influence of distance from the emission source, soil acidity, and local lithogeochemical background on Cu accumulation patterns.

A key controlling factor is the presence of a point-source emitter located within a semi-enclosed mountainous basin. Such geomorphological settings reduce atmospheric dispersion and enhance pollutant retention, promoting long-term soil contamination.

Relief configuration plays a critical role in modulating atmospheric transport processes. Valley morphology, bounded by mountain ranges, limits air exchange and enhances deposition of particulate-bound metals in adjacent low- and mid-altitude zones.

Meteorological conditions, particularly the wind regime and atmospheric stability, are also decisive factors, according to Elminir (2005), Vieira et al. (2006), and Alkama et al. (2009). Prevailing winds in the study area are predominantly from the western direction, which determines the main vector of pollutant transport toward the eastern part of the valley. Calm atmospheric conditions (34% annually, reaching 65% in winter) and frequent temperature inversions further enhance deposition and reduce vertical dispersion of pollutants (Tishkov et al. 1991).

The temporal evolution of industrial emissions, including the transition from high-emission conditions in the late 20th century to improved emission controls in the 21st century, introduces a complex temporal signal in soil contamination. This raises questions regarding the persistence of historically deposited Cu and its long-term retention in surface soils.

An additional challenge is the separation of anthropogenic inputs from natural geochemical background variability in areas with elevated lithogeochemical baseline values.

Finally, Cu persistence is enhanced under acidic soil conditions due to its interaction with soil sorption complexes, resulting in long residence times and limited mobility.

Study area

The study area comprises the eastern part of the Zlatitsa–Pirdop Valley (Western Bulgaria), which is impacted by long-term atmospheric emissions from the Aurubis Bulgaria copper smelter and is located between Zlatitsa and Pirdop.

The valley is a semi-enclosed depression bordered by the Balkan Mountains (north), Sredna Gora Mountains (south), and Koznitsa Hills (west). Elevation ranges from 700 to 1000 m a.s.l., and complex relief significantly influences atmospheric circulation and pollutant dispersion.

Topographic confinement enhances pollutant accumulation by limiting air exchange. The regional climate is temperate continental, with pronounced seasonal variability. The wind regime plays a dominant role in determining pollutant transport pathways, with prevailing western winds directing emissions toward the eastern valley sector.

Calm conditions and frequent temperature inversions further enhance atmospheric stability, promoting deposition of fine particulate matter.

The Aurubis Bulgaria smelter represents the main anthropogenic source of Cu emissions in the region. Since its establishment in 1958, the facility has undergone significant technological modernization, particularly after 1997, including advanced gas-cleaning systems (2006–2016). Despite emission reductions, historical deposition has resulted in long-term soil contamination.

Sampling design

Soil samples were collected along an eastward transect extending from the Aurubis Bulgaria smelter into the eastern part of the Zlatitsa–Pirdop Valley (Fig. 1). The sampling sites are characterized predominantly by grassland, meadow, and pasture ecosystems with no intensive agricultural management, with the exception of a single cultivated garden plot amended mainly with organic manure-based fertilizers.

Sampling targeted the surface soil horizon (0–5 cm), which is most directly affected by atmospheric deposition of particulate-bound contaminants. At each site, composite samples were prepared from multiple subsamples collected within a 5 m radius to minimize local-scale heterogeneity and ensure representativeness.

Soil sampling was conducted during three campaigns (1973, 1995, and 2021), enabling a 48-year temporal assessment of Cu accumulation. Identical sampling locations were used across all campaigns to ensure spatial and temporal comparability. Sampling sites were georeferenced using a handheld GPS device with sub-meter accuracy. All samples were stored in polyethylene bags and transported to the laboratory for further processing.

In the distal part of the linear transect (sites 7–11), sampling density was intentionally increased, as this sector coincides with a zone of slope gradient change and a transition to higher hypsometric levels (Fig. 1). This design was applied to improve spatial resolution in the analysis of geochemical variability associated with topographic heterogeneity.

The main objective of this sampling design was to assess the lateral migration of Cu along the slope—from higher toward lower hypsometric positions—as part of downslope transport and secondary redistribution processes within the soil system. This approach enables evaluation of the horizontal component of element migration, which is essential for interpreting post-depositional behavior of Cu in mountain–valley environments.

In addition, the increased sampling density in this sector allows for the assessment of potential influences of geological variability on Cu distribution. Differences in lithology and weathering intensity may significantly affect both the accumulation and mobility of Cu, thereby contributing to observed spatial anomalies.

Thus, the denser sampling scheme in the terminal part of the transect provides a higher-resolution framework for evaluating the interaction between relief, geological substrate, and lateral Cu migration within the studied system.

The collected samples were air-dried at room temperature, gently disaggregated, and sieved through 0.25 mm and 0.149 mm sieves prior to chemical analysis.

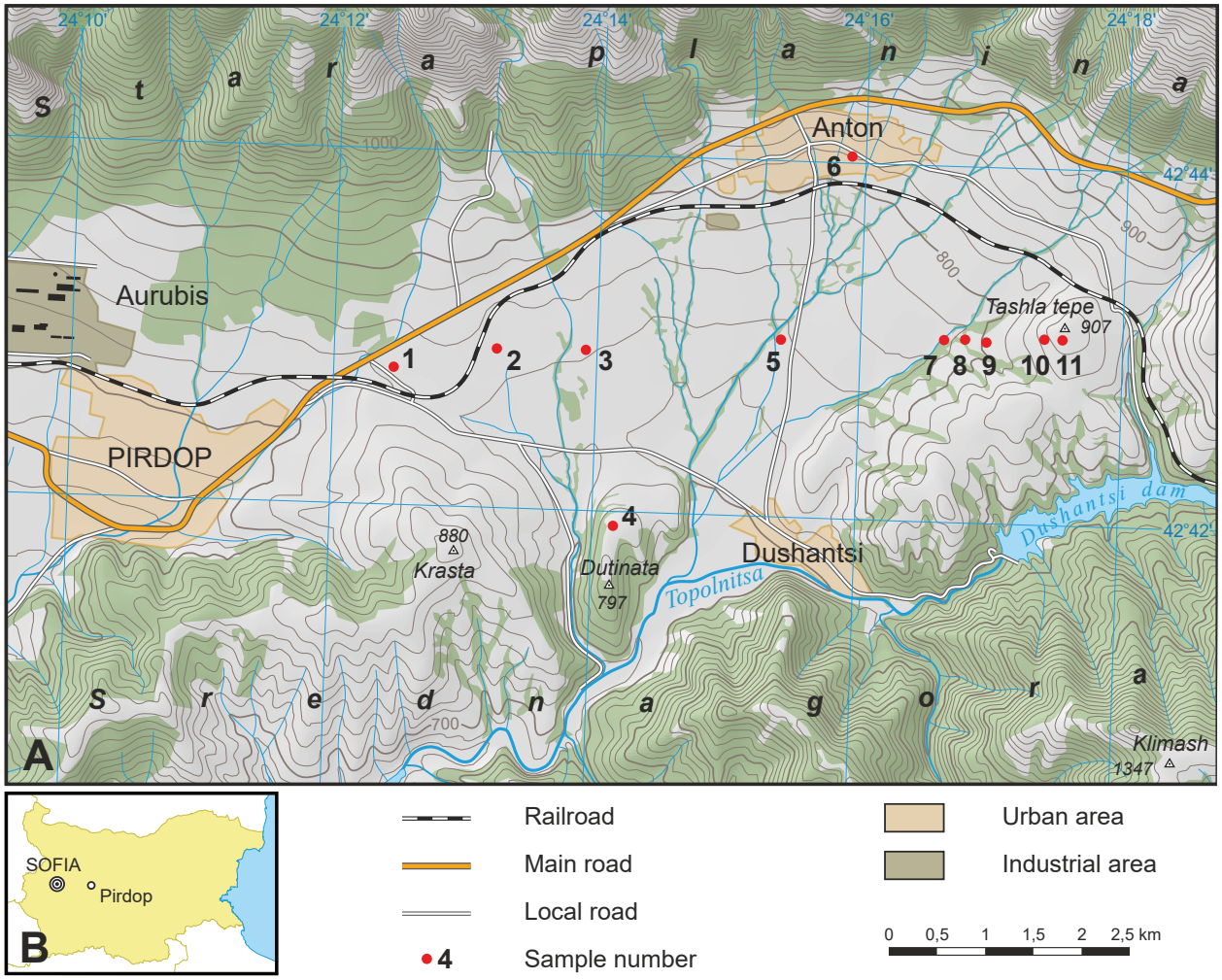

Figure 1. Map of the study area and sampling points.

Soil physicochemical properties, including pH, electrical conductivity (EC), soil organic matter (SOM), carbonate content, and particle-size distribution, were determined using standard analytical procedures. Soil pH and EC were measured in a soil-water suspension (1:2.5), while SOM was quantified using the Walkley–Black method.

Chemical analysis

Determination of total recoverable Cu in soil samples was performed using standardized acid digestion procedures followed by instrumental analysis.

For the 1973 and 1995 datasets, Cu was extracted using aqua regia (HCl:HNO_3, 3:1 v/v) and quantified by flame and electrothermal atomic absorption spectrometry (AAS; PerkinElmer AAS 3030). For the 2021 samples, approximately 0.5 g of air-dried soil was digested using aqua regia in a microwave-assisted system (MARS Xpress, CEM Corporation) under a two-stage temperature program (0–165 °C and 0–175 °C), following ISO 11466. After digestion, samples were subjected to slow oxidation of organic matter, diluted to 50 mL with deionized water, and analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES; Jobin Yvon Ultima 2, 40.68 MHz).

The use of different analytical techniques and instrumentation across the three time periods reflects the evolution of available laboratory methodologies over the 48-year study interval and represents an unavoidable characteristic of long-term environmental datasets. AAS and ICP-OES are both well-established, widely validated techniques routinely applied in environmental geochemistry for trace metal determination, and both are based on internationally recognized analytical principles.

Although ICP-OES generally provides improved sensitivity and multi-element capability compared to AAS, all applied methods are considered fit for purpose for Cu determination in soil matrices and fall within accepted analytical standards for their respective periods. Differences in digestion procedures and detection systems may introduce some variability related to extraction efficiency and matrix effects; however, these are inherent to any long-term dataset compiled over multiple decades.

Importantly, the study does not rely solely on absolute concentration values. Instead, interpretation is based on relative metrics (concentration coefficients, spatial gradients, and temporal trends), which are less sensitive to systematic methodological differences. This approach significantly reduces potential bias arising from analytical heterogeneity.

Therefore, while methodological differences between datasets are acknowledged, they do not compromise the validity of the observed spatial and temporal patterns. On the contrary, they reflect the realistic constraints of long-term environmental monitoring and strengthen the relevance of the dataset by integrating historically consistent, standardized analytical approaches across different time periods.

Data treatment and pollution indices

The study tested the hypothesis that Cu concentrations differ significantly among the three time periods (1973, 1995, and 2021) and are influenced by distance from the emission source, soil properties, and lithogeochemical background.

Soil contamination was assessed using the concentration coefficient (Kc), calculated as the ratio between measured Cu concentrations and local geochemical background values, following Penin (2003).

Temporal variability was evaluated using a time coefficient (Kt), with Cu concentrations in 1973 used as the baseline reference:

$$\mathrm{Kt} = \frac{\mathrm{Ci}(1995 \text{ or } 2021)}{\mathrm{Cf}(1973)},$$

where Ci(t) represents Cu concentrations in 1995 or 2021.

The resulting indices were further interpreted in relation to global soil reference values (Kabata-Pendias and Pendias 2011), European background levels (Salminen et al. 2005), and national geochemical benchmarks for technogenic environments (Penin 2003) (Table 2).

A paired repeated-measures statistical design was applied to evaluate temporal changes in Cu concentrations at identical sampling locations across the three monitoring campaigns (1973, 1995, and 2021). This approach enables

the assessment of site-specific temporal trends in soil contamination while controlling for spatial heterogeneity.

Results

Copper concentrations in surface soils of the eastern Zlatitsa–Pirdop Valley exhibit strong spatial and temporal variability across the three investigated periods (1973, 1995, and 2021) (Table 1).

Since soil sampling was conducted at identical spatial locations (repeated field sampling points), the dataset has a paired structure over time, allowing the assessment of Cu changes at the same sites across different time periods.

In 1973, the highest Cu concentrations were recorded in soils adjacent to the metallurgical plant, with a clear decreasing gradient with distance. The most distal site (9.7 km) showed concentrations below local background values (Fig. 3; Table 2).

In contrast, during 1995 and 2021, elevated Cu concentrations were also detected in the distal parts of the transect, including sites located up to 10.5 km from the emission source (Tashla Tepe sector, 907 m a.s.l.). In 2021, sites 9–11 showed higher Cu concentrations than those situated closer to the smelter (sites 1–2 at 3.65 km), indicating a non-monotonic spatial distribution pattern (Table 1; Fig. 1). Although Cu concentrations generally decreased in 2021 compared to 1995, they remained elevated relative to background levels (Fig. 3; Table 2).

Table 1. Copper content in the soils of the study area, in mg/kg.

Number	Land use	Distance from the source of pollution (km)	Depth in cm	Copper content in 1973 (according to Chuldzyan and Hinov 1976)	Copper content in 1995(according to Penin and Nikolova 1999)	Copper content in 2021
1	Meadow	3.65	0–5	257		84.3
2	Meadow	4.7	0–5	266	337	96.7
3	Meadow	5.6	0–5	171	239	198.2
4	Pasture	6.4	0–5	32	141	155.9
5	Meadow	7.6	0–5	48	147	126.8
6	Arable land	8.4	0–5	70	400	175.6
7	Meadow	9.2	0–5	46	265	117.7
8	Pasture	9.5	0–5		103	67.4
9	Pasture	9.7	0–5	40	84	118.1
10	Pasture	10.3	0–5		234	114.7
11	Pasture	10.5	0–5		381	118.7

Table 2. Copper content in the soils of the world according to Kabata-Pendias and Pendias (2011), in the surface horizons of soils in Europe according to Salminen et al. (2005), in the soils of Bulgaria according to Mirchev (1971), in the soils of technogenic regions of the country according to Penin (2003), and in the local geochemical background according to Velikov and Penin (1994).

Element	Soils of the world (median)	Surface horizon—soils in Europe (median)	Soils in Bulgaria (average)	Soils in technogenic regions in Bulgaria (average)	Local geochemical background (average)
Cu	38.9	13	30	72	125

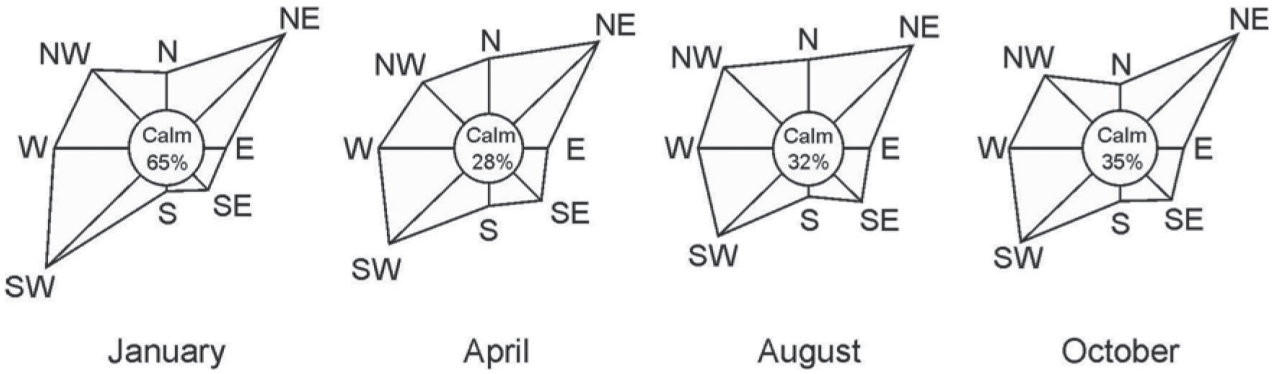

Figure 2. Prevailing wind direction and percentage of calm weather at Pirdop station (according to Tishkov et al. 1991).

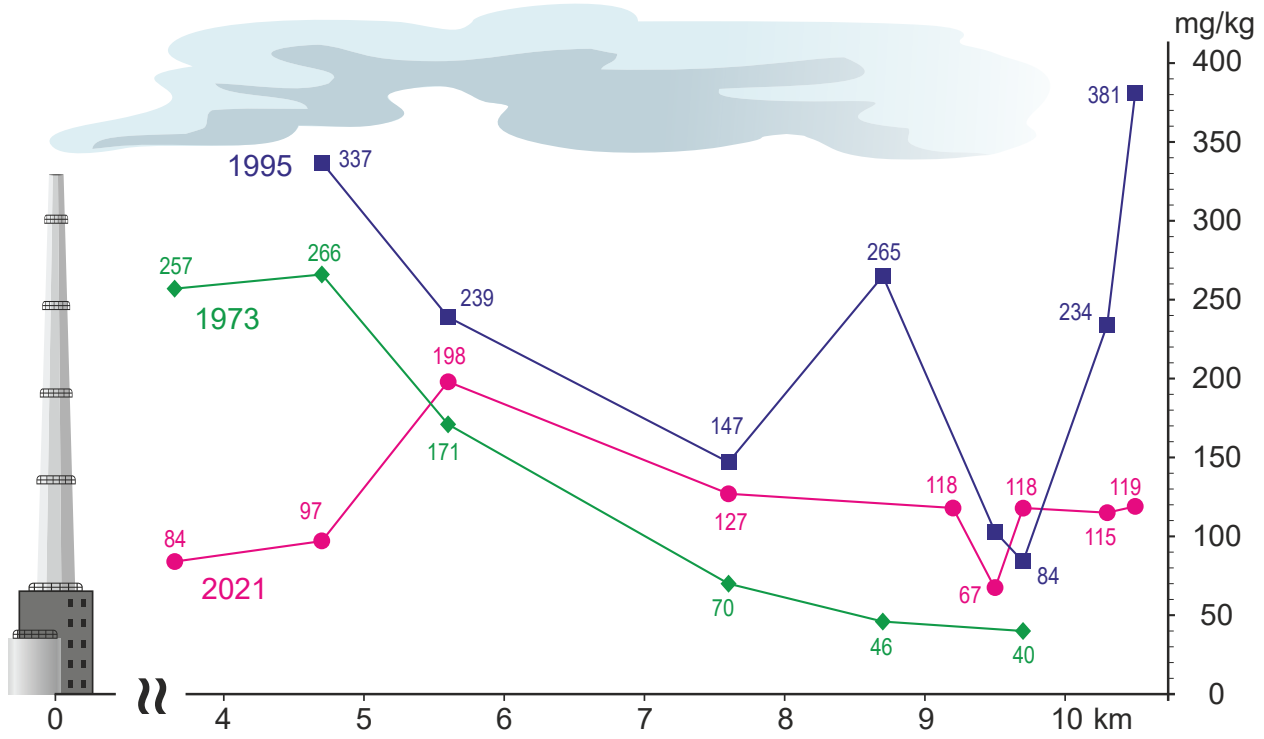

Figure 3. Copper content in the surface horizon of the soils in 1973, 1995 and 2021.

Across all periods, Cu concentrations exceeded reference values for world soils, European topsoils, and Bulgarian technogenic soils (Table 2). The highest enrichment occurred in 1995 (sample 6), reaching up to 5.5 times the average values for technogenic soils in Bulgaria.

Enrichment factors relative to world soils ranged from 1.0 to 6.6 (1973), 2.2 to 10.3 (1995), and 1.7 to 5.1 (2021), while those relative to European soils reached 2.5 to 20.5, 6.5 to 30.8, and 5.2 to 15.2, respectively.

Exceedances of the local geochemical background were identified in 16 of 29 samples, with values ranging from 1.3 to 3.2 times the background level. The temporal concentration coefficient indicates a clear trend of progressive accumulation, particularly over the periods 1973–1995 (1.3–5.7) and 1973–2021 (2.5–5.0) (Fig. 4).

The temporal concentration coefficient (Kt) further confirms a substantial increase in Cu accumulation between 1973 and 1995, reaching up to 5.7-fold

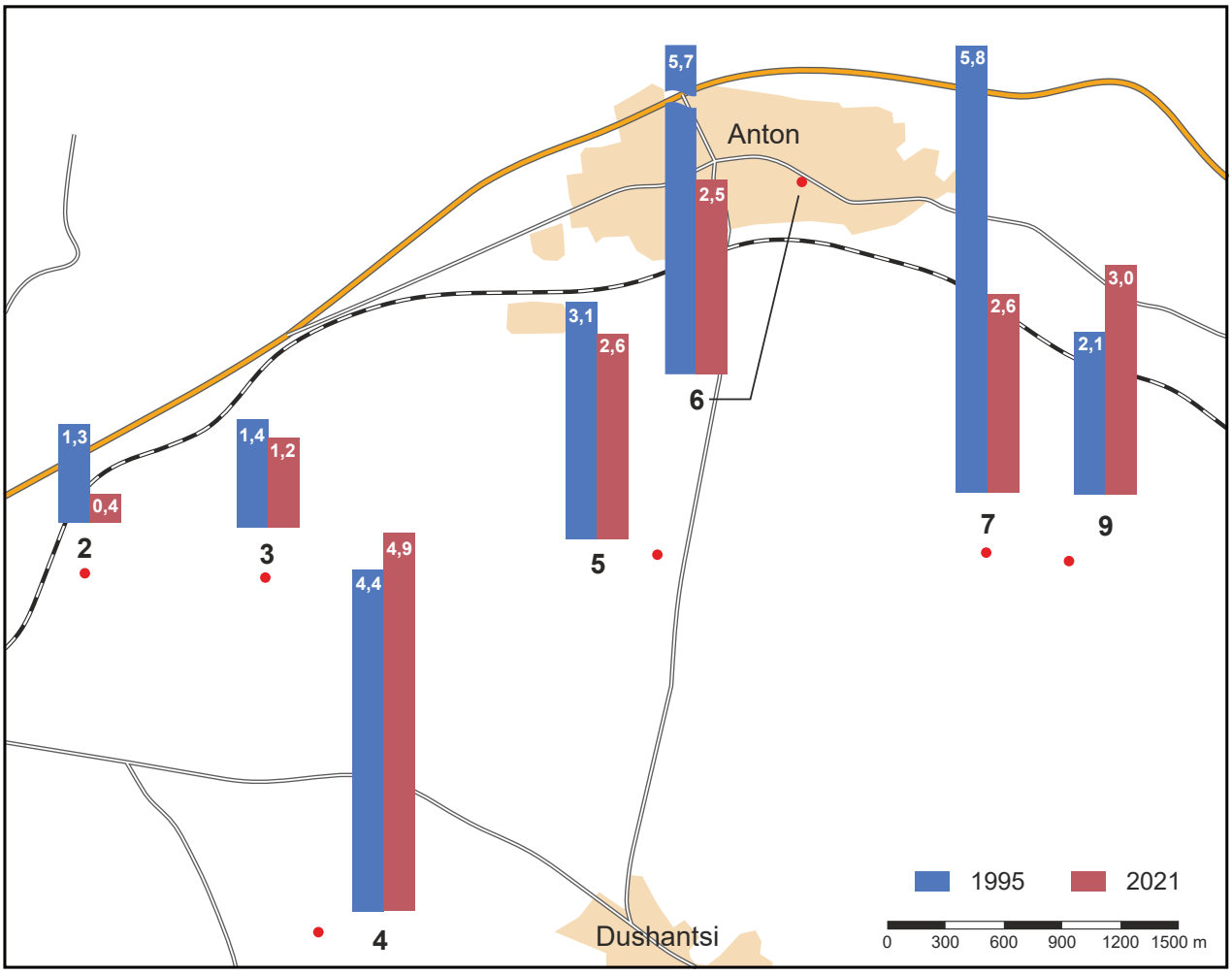

Figure 4. Time coefficient of concentration for the periods 1973–1995 and 1973–2021.

at individual sites. Over the full study period (1973–2021), the increase ranges from 2.5 to 5 times, depending on location. The highest overall Cu concentrations were recorded in 1995, while a general decreasing trend is observed in 2021, particularly at sites located in close proximity to the smelter (Fig. 4).

Soil pH in the study area (2021 data) ranges from 4.3 to 5.9, indicating acidic conditions. Such conditions are relevant for Cu speciation and mobility, favoring the presence of more bioavailable forms in the soil solution.

Discussion

The obtained results reveal a complex interplay between anthropogenic emissions, atmospheric transport processes, and natural geochemical background controlling the spatial and temporal distribution of copper in soils of the Zlatitsa–Pirdop Valley.

A key finding of the study is the temporal transformation of the spatial contamination pattern. In the initial stage of industrial activity (1973), copper distribution exhibits a classical near-source decay pattern, where concentrations decrease sharply with distance from the smelter. This behavior is typical for deposition dominated by low-stack emissions and limited atmospheric dispersion.

However, the spatial pattern observed in 1995 and 2021 deviates significantly from this classical gradient. Elevated copper concentrations are detected at greater distances, and in some cases, higher values occur in distal sites compared to locations closer to the emission source. This indicates a transition from a purely proximity-controlled deposition regime to a more complex dispersion system influenced by higher emission release heights and enhanced atmospheric transport.

The results suggest that the installation of a higher chimney and subsequent technological modifications at the smelter have altered the vertical dispersion of emissions, allowing finer particulate matter to be transported over longer distances. Consequently, contamination is no longer restricted to the immediate vicinity of the plant but is redistributed across the valley system.

Topography plays a critical amplifying role in this process. The enclosed structure of the valley, combined with prevailing western wind directions, facilitates directional transport of pollutants toward the eastern part of the study area. Additionally, frequent calm conditions and thermal inversions enhance atmospheric stability, promoting deposition of fine particulate matter.

Another important factor is the influence of local lithogeochemical background, which appears to contribute significantly to the observed copper levels. In several sampling sites, copper concentrations approach or exceed values attributable to anthropogenic input alone, indicating a mixed geogenic–anthropogenic signal. This complicates the spatial interpretation of contamination and highlights the importance of baseline geochemical characterization in environmental assessments.

Alkaline-acid conditions, expressed as pH, are also important for the accumulation of copper in the surface horizon of the soil. In the region, pH varied between 4.3 and 5.9 in 2021, which defines the environment as slightly to moderately acidic. Thus, the available alkaline-acid (pH) conditions predispose copper to relative activity, which leads to the overall copper pollution of landscapes. When studying the behavior of copper in the soil, it should be taken into consideration that it is a relatively mobile chemical element and participates in reactions with the soil uptake complex while being actively extracted by plant and microbial organisms. The main forms of Cu migration at pH < 7 are $CuOH^{+}$ and $Cu_2(OH)_2$ Romić et al. (2014).

According to Ding et al. (2023), the spatial heterogeneity of contamination is associated both with the atmospheric transport of emissions and with local soil properties. The authors further report that acidic soil conditions and iron oxides play a key role in the mobility and transformation of metals within the soil environment.

From a temporal perspective, the calculated concentration coefficients indicate that copper accumulation is persistent over decadal time scales. Despite significant reductions in atmospheric emissions following industrial modernization and implementation of advanced gas-cleaning systems, previously deposited copper remains largely retained in the upper soil horizon. This confirms the low mobility and long environmental residence time of copper in acidic soil conditions. According to Adriano (2005) and Aponte et al. (2021), Shishkov and Hristov (2016), long-term contamination by Cu and associated metalloids significantly alters soil microbial functional diversity and enzyme activity, indicating persistent impacts of smelter-derived pollution on soil ecological functioning.

These findings are consistent with previous studies on smelter-related contamination, which emphasize the long-range transport of particulate-bound metals and their long-term persistence in soil systems. However, the present

study extends this knowledge by providing a multi-decadal temporal framework that captures both the pre- and post-modernization phases of industrial activity.

Overall, the results demonstrate that soil contamination in the study area is controlled by a combination of historical emission intensity, atmospheric dispersion conditions, and landscape-specific factors. This reinforces the necessity of integrating temporal evolution into environmental risk assessments rather than relying solely on current emission levels.

Conclusion

The present study investigated the long-term influence of atmospheric emissions from a copper smelter on the spatial distribution and temporal evolution of copper concentrations in soils within the eastern part of the Zlatitsa–Pirdop Valley over a 48-year period (1973–2021).

The results demonstrate that the spatial pattern of copper accumulation has undergone a pronounced transformation through time, reflecting changes in emission intensity, emission height, and atmospheric dispersion conditions. During the initial stage of industrial activity (1973), copper distribution exhibited a strong near-source gradient, with concentrations decreasing rapidly with increasing distance from the smelter, indicating predominantly localized deposition.

In contrast, the later investigation periods (1995 and 2021) reveal a substantially different spatial configuration, characterized by the persistence of elevated copper concentrations at greater distances from the emission source. In some locations, concentrations exceeded those recorded in proximal areas. This pattern indicates a transition from localized contamination toward a more regionally dispersed pollution system, controlled primarily by atmospheric transport processes and modified emission release conditions, particularly the increase in chimney height and technological changes in metallurgical production.

The observed distribution of copper is additionally influenced by the combined effects of topographic confinement within the valley, prevailing wind circulation, frequent atmospheric stability and inversion conditions, and the naturally elevated local lithogeochemical background. The interaction between anthropogenic deposition and geogenic background enrichment contributes significantly to the long-term persistence of high copper concentrations in surface soils.

From a temporal perspective, the study confirms that copper behaves as a persistent and relatively immobile contaminant within the upper soil horizon, exhibiting very slow natural attenuation over decadal time scales. Despite reductions in industrial emissions following technological modernization, historically accumulated copper remains retained in soils, demonstrating a strong long-term environmental memory of past industrial activity.

The continuous exceedance of regulatory threshold values throughout all investigated periods indicates that copper contamination in the study area represents not only a historical legacy but also a constant environmental pressure. The potential ecological implications extend beyond soil degradation alone and may include the gradual transfer of heavy metals into adjacent ecosystems, groundwater systems, and trophic chains.

Overall, the results demonstrate that soil contamination in the investigated region is controlled not only by present-day emissions but also by cumulative historical deposition and landscape-specific environmental conditions. This

highlights the necessity of incorporating long-term temporal analyses into environmental assessments of industrial regions.

The findings contribute to a better understanding of the long-term dynamics of heavy metal contamination in mountainous industrial landscapes and provide a scientific basis for improving environmental monitoring programs, pollution risk assessments, and future remediation and land-management strategies.

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Additional information

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The authors have declared that no competing interests exist.

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Data availability

All of the data that support the findings of this study are available in the main text.