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SOIL METAL CONTAMINATION AND POLLUTION INDICES IN THE VICINITY OF A NON-FERROUS METAL SMELTER, PLOVDIV (BULGARIA)

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Abstract

Mining and smelting of metal ores are among the major anthropogenic activities contributing to environmental pollution, particularly through the release of toxic metals into surrounding soils. This study investigates the extent, intensity, and spatial distribution of heavy metal contamination in soils surrounding the Non-Ferrous Metal Smelter (KCM–Plovdiv) in southern Bulgaria. Total concentrations of Pb, Zn, and Cd were measured and compared with national and international soil quality standards, including the Bulgarian Regulation No. 3, WHO reference values, and the Dutch Maximum Allowable Concentrations (MAC) and Intervention Concentrations (IC). Several contamination indices were applied, including the geoaccumulation index (Igeo), contamination factor (CF), pollution load index (PLI), and Nemerow index (NPI).

The results revealed extremely high metal concentrations, with maximum values of 28,162 mg/kg for Pb, 10,596 mg/kg for Zn, and 528.8 mg/kg for Cd. A pronounced spatial gradient was observed, with the highest contamination within 500 m of the smelter chimney. Contamination was largely restricted to the topsoil (0–20 cm), reflecting limited vertical mobility of Pb and Cd. Integrated indices (PLI, NPI) confirmed severe to extreme pollution across most of the study area, with NPI values exceeding 190 at several hotspots. These findings demonstrate large-scale, long-term heavy metal pollution and emphasize the need for remediation and continuous monitoring.

Keywords: cadmium, pollution indices, soil contamination, lead, zinc, smelter

INTRODUCTION

Heavy metal pollution of soils is a major environmental concern worldwide, particularly in areas impacted by mining, smelting, and other industrial operations. Unlike organic pollutants, heavy metals are non-biodegradable and persist in the environment for decades, accumulating in soils, sediments, plants and biota (Adriano, 2001; Alloway, 2013). Elevated concentrations of lead (Pb), cadmium

(Cd) and zinc (Zn) are known to reduce soil fertility, degrade agricultural productivity, and cause severe health effects through inhalation, ingestion or transfer along the food chain (Kabata-Pendias & Mukherjee, 2007; Wuana & Okieimen, 2011).

Non-ferrous metal smelters represent some of the largest anthropogenic sources of airborne particulate emissions enriched in heavy metals. Fine metalliferous particles can be transported over long distances and deposited in surrounding soils, producing strong spatial gradients typically decreasing with distance from the emission source (Wong et al., 2013). The Non-Ferrous Metal Smelter KCM–Plovdiv in southern Bulgaria is among the largest metallurgical complexes in southeastern Europe, and multiple studies have documented enhanced Pb, Cd and Zn deposition in its vicinity (Angelova et al., 2010). Although technological improvements have reduced recent emissions, legacy pollution remains extensive and environmentally significant.

A critical challenge in assessing soil contamination is the ability to distinguish between lithogenic (natural) and anthropogenic (industrial) metal contributions. Parent rock composition, geochemical anomalies and mineralogy may lead to naturally elevated metal levels. Thus, total concentrations alone cannot determine the origin of contamination (Reimann & de Caritat, 2005). To address this, environmental geochemistry relies on contamination indices that characterize pollution intensity, origin, and ecological relevance.

The Geoaccumulation Index (Igeo) (Müller, 1969) compares present concentrations to pre-industrial baselines, identifying anthropogenic enrichment. Additional indices quantify pollution magnitude: the Contamination Factor (CF) evaluates enrichment relative to background values, while integrative indicators such as the Pollution Load Index (PLI) (Tomlinson et al., 1980) and the Nemerow Index (NPI) provide cumulative assessments of multi-metal contamination, identify hotspots and guide remediation.

Even in areas where contamination is evidently severe, such indices remain essential because they contextualize chemical data, quantify contamination severity, reveal spatial and atmospheric deposition patterns, and allow comparison across industrial regions. They transform concentration measurements into actionable environmental information, enabling informed environmental management and risk assessment.

Given the long history of smelting activities at KCM–Plovdiv and persistent reports of heavy metal emissions, the present study integrates chemical analysis with multiple contamination indices to characterize soil pollution, its spatial distribution, ecological implications, and potential health risks.

MATERIALS AND METHODS

The study was conducted in the vicinity of the Non-Ferrous Metal Smelter KCM–Plovdiv, one of the largest Pb–Zn metallurgical complexes in southeastern Europe. The area includes agricultural land, suburban settlements, and industrial zones. The climate is transitional-continental, with annual precipitation of 450–550 mm and prevailing west–southwest winds, which strongly influence the atmospheric transport and deposition of metal-rich particulates emitted from the smelter.

Nineteen composite topsoil samples (0–20 cm) were collected following ISO 10381-1 (2002). Sampling sites were located at distances of 100, 500, 1000, 3000, 5000 and 10000 m from the smelter chimney. Each composite sample consisted of five subsamples collected within a 5 × 5 m grid. Samples were stored in polyethylene bags and transported to the laboratory for analysis.

Samples were air-dried, gently homogenized, and sieved to <2 mm. Total pseudo-total metal concentrations (Pb, Cd, Zn) were determined by aqua regia digestion following ISO 11466 (1995), using a mixture of HCl and HNO_3 (3:1). Digests were analyzed using Atomic Absorption Spectrometry (AAS) with adequate calibration standards.

Background concentrations (Bn) for Pb, Cd, and Zn were based on regional geochemical datasets for Bulgarian soils and southeastern Europe (Kabata-Pendias & Mukherjee, 2007; Alloway, 2013).

Multiple geochemical indices were calculated to: (1) determine contamination severity, and (2) assess cumulative pollution.

Geoaccumulation Index (Igeo) (Müller, 1969)

$$Igeo = log_2(\frac{Cn}{1.5XBn})$$

Where: C_n – measured concentration of the metal; B_n – background concentration; 1.5 – correction factor accounting for natural variability Igeo values classify soils into seven contamination classes (0–6).

Contamination Factor (CF) (Hakanson, 1980)

$$CF = \frac{Cn}{Bn}$$

Classification: CF < 1 = low contamination; 1–3 = moderate; 3–6 = considerable; 6 = very high contamination

Pollution Load Index (PLI) (Tomlinson et al., 1980)

$$PLI = (CFPb\ X\ CFZn\ X\ CFCd)^{1/3}$$

A single value representing overall soil quality. PLI > 1 indicates polluted soil.

Nemerow Pollution Index (NPI) (Nemerow, 1985)

$$NPI = \frac{\sqrt{CFmean^2 + CFmax^2}}{2}$$

The index integrates both the average and the maximum contamination intensity, thus reflecting combined pollution pressure. NI > 10 indicates extreme pollution.

Statistical analyses were performed using SPSS v.26.

RESULTS AND DISCUSSION

Descriptive statistics for Pb, Cd, and Zn concentrations in soils are presented in Table 1. The measured values reveal extremely wide concentration ranges, reflecting strong spatial heterogeneity characteristic of atmospheric deposition near non-ferrous smelting facilities. To contextualize the observed concentrations, the results were compared with the threshold values established by

Bulgarian Regulation No. 3 (2008), as well as with internationally recognized reference levels, including WHO guideline values, EU background concentrations, and the Dutch Soil Quality Standards (MAC and IC). The Dutch standards are widely adopted in environmental assessments across Europe due to their explicit differentiation between target (MAC) and intervention (IC) thresholds. Table 2 summarizes these regulatory frameworks and provides a multi-criteria basis for evaluating contamination intensity, ecological risk, and the exceedance of nationally and internationally accepted soil quality limits (VROM, 2013; WHO, 2017).

Table 1. Comparison of soil heavy metal concentrations with the threshold values defined in Bulgarian Regulation No. 3

Element	*Min*	*Median*	*Max*	*MAC (BG)*	*IC (BG)*	*Exceedance (Median/MAC)*	*Exceedance (Max/IC)*
Pb	4.1	2112.4	28161.7	60	300	**35×**	**94×**
Cd	0.6	50.7	528.8	1	5	**50×**	**106×**
Zn	50.3	2449.7	10596.3	140	300	**17×**	**35×**

Table 2. Regulatory threshold values for heavy metals according to Bulgarian Regulation No. 3 (2008), EU reference levels, WHO guidelines, and the Dutch Soil Quality Standards (mg/kg)

Element	*Bulgarian regulatory thresholds*			*Dutch standards*		*WHO soil hazard levels*	*EU background levels*
	PC	MAC	IC	MAC	IC		
Pb	25	60	300	85	530	> 100	15-50
Cd	0.5	1	5	0.8	1.2	> 3	0.1-1
Zn	70	140	300	140	720	> 300	50-150

Preventive Concentrations (PC); Maximum Allowable Concentrations (MAC); Intervention Concentrations (IC).

The concentrations of Pb, Cd, and Zn near the smelter indicate exceptionally severe anthropogenic contamination. A clear spatial gradient is evident, with the highest concentrations occurring within 250–500 m from the metallurgical complex. Beyond approximately 3000 m, the concentrations of all three metals decrease towards background levels, confirming the dominant role of atmospheric deposition originating from the smelter.

Lead (Pb) exhibited the widest concentration range, from 4.1 to 28,161.7 mg/kg, with a median of 2,112.4 mg/kg. The minimum concentration is within natural background levels, suggesting the presence of uncontaminated peripheral soils. In contrast, the median concentration exceeds the Dutch Intervention Concentration (530 mg/kg) by approximately twenty-five times, indicating widespread pollution across the study area. The maximum concentration surpasses the Dutch MAC (85 mg/kg) by more than three hundred times and the IC by over fifty times, values comparable to those reported in the most heavily polluted smelter-affected regions in Europe and China (Ettler, 2016; Jiang et al., 2021). These results identify Pb as the dominant contaminant and confirm its long-term accumulation around the industrial source.

Cadmium (Cd) concentrations ranged from 0.6 to 528.8 mg/kg, with a median of 50.7 mg/kg. The minimum value is close to natural background concentrations, but the median level exceeds the Dutch MAC (0.8 mg/kg) by more than sixty-fold and the Dutch IC (12 mg/kg) by more than four-fold, demonstrating that cadmium contamination is pervasive and severe. The maximum concentration exceeds the MAC by over six hundred times and the IC by more than forty times, values characteristic of soils exposed to intensive emissions from Pb–Zn metallurgical activities.

Zinc (Zn) concentrations varied between 50.3 and 10,596.3 mg/kg, with a median value of 2,449.7 mg/kg. The minimum concentration corresponds to typical EU background values, indicating the presence of relatively unaffected soils in the outer parts of the study area. However, the median concentration exceeds the Dutch MAC (140 mg/kg) by seventeen times and the IC (720 mg/kg) by more than three times. The maximum concentration surpasses the MAC by approximately seventy-five times and the IC by fifteen times. These results confirm intense Zn accumulation in the soils, consistent with deposition patterns observed near Zn/Pb smelting operations in other European industrial regions (Ettler, 2016).

The measured concentrations of Pb, Cd, and Zn exceed all Bulgarian regulatory thresholds (PC, MAC, IC) by wide margins. Median concentrations for all three metals surpass IC values, demonstrating that soil quality in most sampling locations falls into the highest contamination category defined by Regulation No. 3.

When evaluated against international benchmarks, the contamination is similarly extreme. Pb concentrations exceed WHO hazard levels by one to two orders of magnitude and surpass the Dutch IC by more than 50-fold. Cd levels exceed WHO high-risk thresholds by up to 100-fold, while Zn exceeds the Dutch IC by up to 15-fold and Bulgarian IC by more than 30-fold.

Compared with EU baseline values, median Pb, Cd and Zn concentrations exceed natural background levels by factors of 40–500. This confirms that the contamination cannot be attributed to lithogenic variations and is entirely anthropogenic.

Under the Bulgarian soil protection regulation, the exceedance of IC values indicates that urgent risk assessment and remediation actions are required. Since median Pb, Cd and Zn concentrations already exceed the IC values by factors of 7–10, contamination is not limited to discrete hotspots but affects the majority of the study area.

The extremely large differences between minimum and maximum concentrations for all three metals demonstrate strong spatial heterogeneity caused by uneven atmospheric deposition. The presence of highly contaminated hotspots near the smelter chimney, followed by a steady decline in concentrations with distance, indicates a typical pattern of deposition from an elevated point source. The spatial trend is further shaped by prevailing winds and local topography, which influence the distribution and intensity of particulate emissions. The detection of natural or near-background concentrations in the peripheral areas confirms that the contamination is anthropogenic rather than geogenic. This spatial pattern is consistent with findings reported for major non-ferrous smelters in Poland, Germany, Serbia, and China, where similar gradients of Pb, Cd, and Zn are observed (Jiang et al., 2014; Ettler, 2016). The results clearly demonstrate the long-term and large-scale environmental impact of atmospheric emissions from the examined smelter. The detected concentrations of Pb, Cd, and Zn substantially exceed levels associated with ecological and human health risks. According to WHO and EU assessments, such concentrations adversely affect soil microbial activity, inhibit plant growth, and increase the risk of metal uptake into crops (Giller et al., 2009; WHO, 2017). In addition, Pb and Cd pose significant human health hazards through inhalation of contaminated dust and accidental soil ingestion. Since the median concentrations of all three metals already surpass intervention thresholds, the contamination is not restricted to isolated hotspots but instead affects the majority of the studied area. This indicates that the environmental impact of the smelter is both severe and extensive, necessitating targeted remediation measures and long-term monitoring.

The calculated contamination indices provide an integrated evaluation of the severity, origin, and spatial patterns of heavy metal pollution in the soils surrounding the smelter. The Geoaccumulation Index (Igeo) showed that the soils are moderately to heavily polluted with Pb and Cd in the areas closest to the emission source, with several sites falling into the category of extremely contaminated (Fig.1). The Contamination Factor (CF) classified most sampling points within 500 m of the smelter as considerably to highly contaminated, with CF values reflecting the exceptionally elevated metal concentrations determined by chemical analysis (Fig.2).

The Pollution Load Index (PLI) exceeded a value of 1 within a radius of 1500 m around the smelter, demonstrating widespread degradation of soil quality. The distribution of PLI values, ranging from 0.72 to 9.01, with a median of 6.15, further shows that more than half of the soils fall within the categories of strongly to extremely contaminated areas. Only a small fraction of samples exhibited PLI values below 1, indicating minimally affected locations situated primarily at the periphery of the study area (Fig.3).

The Nemerow Pollution Index revealed similar trends, identifying distinct contamination hotspots aligned with the prevailing wind direction. Minimum NPI values were close to background levels, while median values placed the majority of the study area within the category of extremely polluted

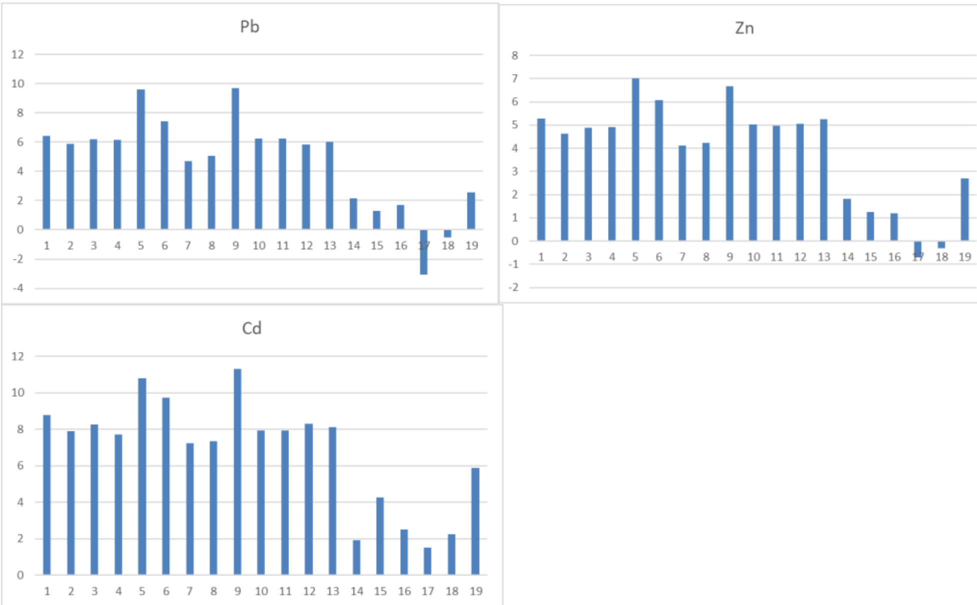

Fig.1. Geoaccumulation Index (Igeo) for Pb, Cd and Zn calculated at all sampling locations.

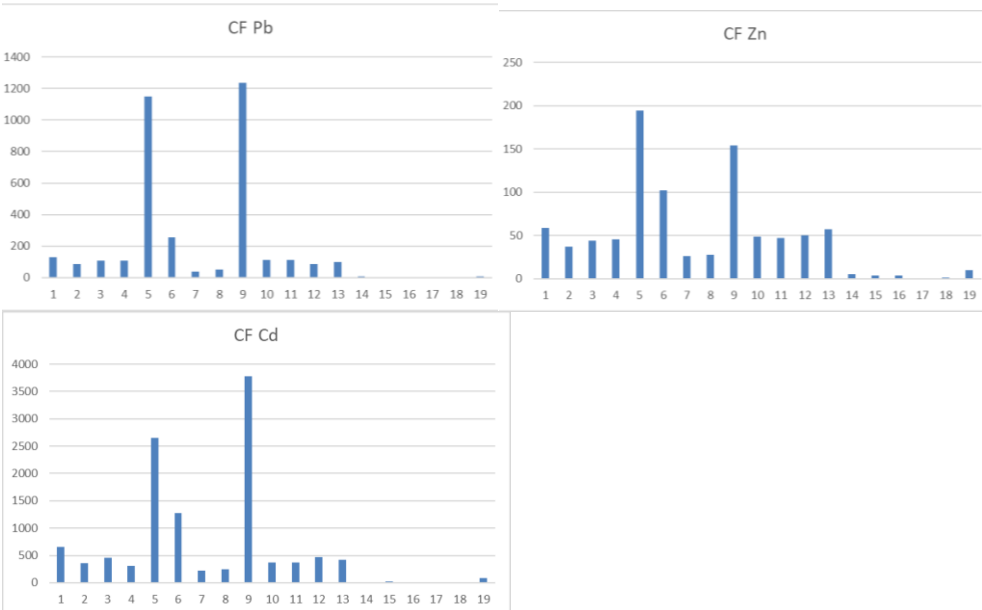

Fig.2. Contamination Factor (CF) values for Pb, Cd and Zn calculated based on regional background concentrations.

Maximum NPI values exceeded 190, reflecting catastrophic levels of contamination that are characteristic only of the world’s most severely impacted smelter regions (Fig.3).

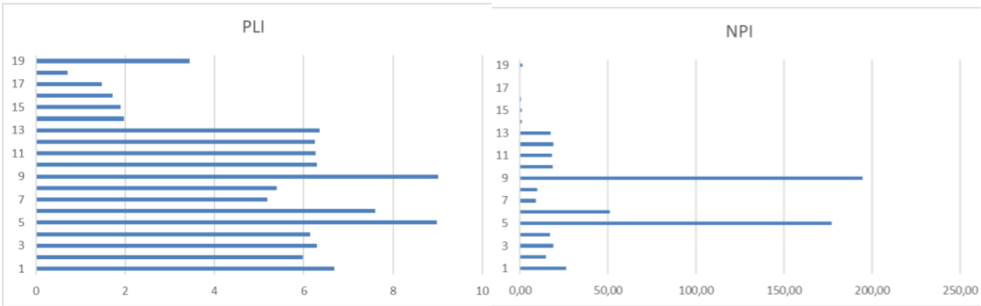

Fig.3. Pollution Load Index (PLI) calculated from the contamination factors (CF) of Pb, Cd and Zn and variation of Nemerow Pollution Index (NPI) based on multi-metal contamination in surface soils

Collectively, the contamination indices provide strong evidence that Pb, Cd, and Zn pollution around the smelter is not only severe but also spatially extensive. They confirm that the contamination is unequivocally anthropogenic, long-term in nature, and primarily driven by atmospheric deposition from smelting activities.

CONCLUSIONS

This study provides an integrated assessment of heavy metal contamination in soils surrounding the Non-Ferrous Metal Smelter KCM–Plovdiv, combining chemical analyses with several single and composite pollution indices. The concentrations of Pb, Cd, and Zn in the topsoil (0–20 cm) are extremely elevated in comparison with Bulgarian Regulation No. 3, WHO reference values, and the Dutch Maximum Allowable (MAC) and Intervention Concentrations (IC). In many locations, measured levels exceed these thresholds by one to two orders of magnitude, indicating long-term and severe anthropogenic impact.

A pronounced spatial pattern was observed, characterized by steeply decreasing concentrations with distance from the smelter. The highest levels of contamination occurred within 500 m of the industrial source. The calculated indices Igeo and CF classify most soils near the smelter as heavily to extremely contaminated, while the Pollution Load Index (PLI) and Nemerow Pollution Index (NPI) identify large areas affected by multi-metal pollution. Maximum NPI values above 190 reflect contamination levels comparable to the most heavily impacted smelting regions reported internationally.

The contamination is largely restricted to surface soils, consistent with atmospheric deposition as the primary source. The presence of near-background concentrations at the periphery confirms the anthropogenic origin of the pollution.

Given the magnitude and persistence of the contamination, targeted remediation and land management strategies are urgently needed. Effective measures may include phytostabilization with metal-tolerant plants, the use of soil amendments to reduce metal mobility, restrictions on agricultural use of highly affected zones, and actions to limit dust resuspension. Long-term environmental monitoring is essential to evaluate ecological risks and track the effectiveness of remediation efforts.

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REFERENCES

Adriano, D.C. (2001). Trace Elements in Terrestrial Environments. Springer.

Alloway, B.J. (2013). Heavy Metals in Soils. Springer.

Angelova V., Ivanova, R., Todorov, J., & Ivanov, K. (2010). Lead, cadmium, zinc, and copper bioavailability in the soil-plant-animal system in a polluted area. *ScientificWorldJournal*, 17(10), 273-285.

Anonymous. (2008). Regulation No. 3 of August 1, 2008 on the norms for the permissible content of harmful substances in soils (State Gazette No. 67/2008).

Ettler, V. (2016). Soil contamination near non-ferrous metal smelters: A review. *Applied Geochemistry*, 64, 56-74.

Giller, K. E., Witter, E., & McGrath, S. P. (2009). Heavy Metals and Soil Microbes. *Soil Biology & Biochemistry*, 41, 2031–2037.

Hakanson, L. (1980). An ecological risk index for aquatic pollution. *Water Research*, 14, 975–1001.

Jiang, Zh., Guo, Zh., Chi Peng C., Liu, X., Zhou, Z., & Xiao, X. (2021). Heavy metals in soils around non-ferrous smelteries in China: Status, health risks and control measures. *Environmental Pollution*, 282, 117038

Kabata-Pendias, A. & Mukherjee, A.B. (2007). Trace Elements from Soil to Human. Springer.

Müller, G. (1969). Index of geoaccumulation. *Geojournal*, 2, 108–118.

Nemerow, N. (1985). Stream, Lake, Estuary and Ocean Pollution (2nd ed.). Van Nostrand Reinhold Publishing

ISO 10381-1 (2002). Soil quality — Sampling — Part 1: Guidance on the design of sampling programmes.

ISO 11466 (1995). Soil quality - Extraction of trace elements soluble in aqua regia.

Reimann, C., & de Caritat, P. (2005). Distinguishing natural and anthropogenic sources of metals. *Science of the Total Environment*, 347, 1–32.

Tomlinson, D. L., Wilson, G., Harris, C. R., & Jeffery, D. W. (1980). Assessment of Heavy Metals Levels in Estuaries and Formation of a Pollution Index. *Helgoländer Meeresuntersuchungen*, 33, 566-575.

VROM (2013). Dutch Soil Quality Standards. Ministry of Housing, Spatial Planning and the Environment, Netherlands.

WHO (2017). Environmental Health Criteria: Lead and Cadmium. World Health Organization.
Wong, C.S.C., Li, X.D., Zhang, G., Qi, S.H., & Peng, X.Z. (2003). Atmospheric deposition of heavy metals in the Pearl River Delta, China. *Atmospheric Environment*, 37 (6), 767-776.
Wuana, R., & Okieimen, F. (2011). Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. *ISRN Ecology*, ID 402647, 1- 20, doi:10.5402/2011/402647