Assessment of Heavy Metal Pollution in Agricultural Soils around Abandoned Kettara Mine in Marrakech, Morocco

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Abstract

This study evaluates heavy metal contamination in agricultural soils surrounding the abandoned Kettara mine near Marrakech, Morocco. A total of 120 soil samples were collected in the impacted zone, along with 6 background samples located 20 km from the mine site. Soil's physicochemical parameters showed slightly acidic pH values (6.7 in KC1 and 6.9 in KC2), elevated electrical conductivity (1706.2 and 1830.4 µS/cm), and increased sulfur content (1.3% and 0.9%), all indicating a potential for enhanced metal mobility. Cadmium, copper, lead, and zinc concentrations reached 2.6, 427.8, 384.0, and 756.4 mg·kg^{-1} respectively in KC1 and remained substantially elevated in KC2 compared to background levels. Contamination factors and pollution index values, ranging from 5.2 to 32.5 for CF and from 55.1 to 48.9 for PI in KC1 and KC2, respectively, confirm significant anthropogenic pollution. The lack of mitigation measures for mine tailings has contributed to ongoing soil contamination, posing risks to surrounding rural communities with serious implications for environmental and agricultural sustainability. These findings emphasize the urgent need for effective environmental management and remediation strategies .to address the ecological and public health impacts of mining pollution

1. Introduction

As a result of human and natural activities, the introduction of metallic pollutants into the environment has become a major concern due to their adverse effects globally (Sumanta et al., 2023; Briffa et al., 2020). The expanding industrialization and economic growth, coupled with the production and consumption of various compounds and chemicals, have led to the generation of dangerous pollutants that pose serious risks to the environment and human health (Ranjeet et al., 2023; Md Golam et al., 2023). Natural events, such as soil and rock weathering, earthquakes, and floods, also contribute to environmental pollution (Anthony and Rusyn, 2016; Espinoza-Quiñones et al., 2005). Additionally, the improper disposal of municipal, industrial, and agricultural waste further exacerbates environmental pollution caused by human activities (Al-Hanini et al., 2024).

Industrial processes, including mining and smelting operations, have been identified as significant sources of hazardous metals in the environment (Muhammad et al, 2024; Barkouch et al., 2024; Pruvot et al., 2006). Mining operations, encompassing mineral excavation, ore transportation, smelting and refining processes, and the disposal of tailings and waste water, are significant sources of heavy metal contamination in the vicinity of mines (Haghighizadeh et al., 2024; Hosseinpour et al., 2022). Mine residues, deposited

on surrounding soils, are exposed to abiotic environmental factors, such as rain and wind, which mobilize the metallic content of the waste into the environment (Guillevic et al., 2023; Ping et al, 2019). This mobilization can lead to soil contamination with trace metals and the generation of acid mine drainage, disrupting the stability and renewal of natural ecosystem resources. Consequently, contamination from mine tailings can impact not only the immediate mining sites but also extend to larger areas, including surface waters and agricultural soils (Ifeanyi and Yusuf, 2023).

Several studies have examined the impact of mining on environmental pollution in Morocco, particularly in regions near abandoned mining sites. For instance, a study identified significant contamination of soils and crops with metals such as lead, cadmium, and zinc in areas surrounding mining operations (Valiente et al., 2012). Its findings support the need for continued monitoring and management of mining activities in these regions. Similar studies have reported high concentrations of heavy metals in soils near mining districts in Morocco, reinforcing the potential risks posed by such activities to both the environment and human health (El Haya et al., 2023; Barkouch and Pineau, 2016).

The environmental consequences of excessive heavy-metal dispersion from mine and smelter sites include water and soil contamination, phytotoxicity, soil erosion, and potential risks to human health. These pollution consequences arise

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when mobilized and bioavailable trace metals are absorbed by plants or transported to groundwater aquifers (Kafle et al., 2022).

Abandoned and active mines are often linked to elevated concentrations of heavy metals in surrounding areas due to the discharge and dispersion of untreated waste materials into nearby agricultural soils, food crops, riverine waters, and stream sediments (Bany Yaseen and Al-Hawari, 2019; González-Martíne et al., 2019; Liu et al., 2005; Lu and Zhang, 2005). This widespread soil contamination with heavy metals from mines has raised significant environmental concerns (Kachenko and Singh, 2006). In this context, high soil metal contamination and severe accumulation of trace elements in crops have been reported in both operational and abandoned mining districts in the Marrakech region of Morocco (El Haya et al., 2023; Barkouch and Pineau, 2016). Similarly, certain crops, cultivated near mining sites in this region, have been found to contain lead and cadmium at concentrations exceeding permissible limits. This contamination impacts the food chain, leading to health problems in both humans and animals (El Haya et al., 2023; Mashal et al., 2017; Barkouch and Pineau, 2016).

Given the urgency of the situation, it is essential to assess the distribution of heavy metals in surface soils, which serve as crucial sinks for pollutants, to understand the overall status of heavy metal pollution and its associated ecological risks in the region. The results of such assessments are vital for effective environmental management in areas undergoing rapid industrial transformation.

The objective of this study is to evaluate the impact of mining activities on heavy metal concetrations in agricultural soils in the vicinity of the Kettara mine in Marrakech,Morocco and to compare the findings with those from a control site. By shedding light on the potential impacts of pollutants, this study aims to raise awareness and provide valuable insights for the efficient management of surface soil quality in the mining area.

2. Materials and Methods

2.1. Site description

The abandoned Kettara mine is situated approximately 30 km northwest of Marrakech, within the heart of the central Jebilet Mountains in Southern Morocco (Figure 1) (Hakkou et al., 2008).
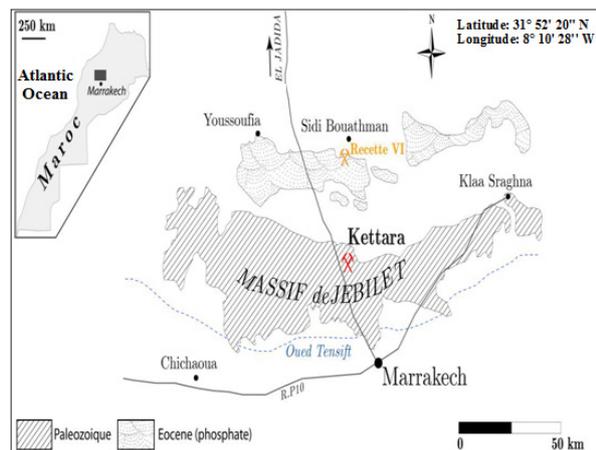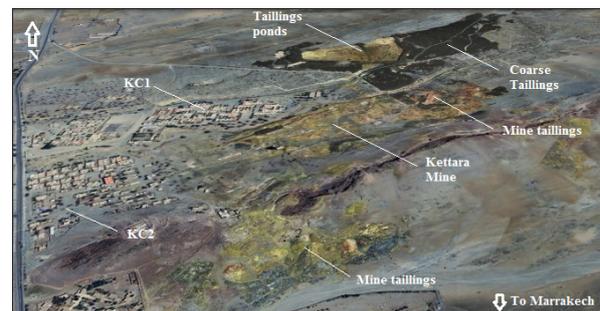

Figure 1. Geographic situation of the Kettara mine in the Marrakech region.

Active mining operations at the Kettara mine occurred between 1964 and 1981, primarily extracting pyrrhotite, with a total production exceeding 5.2 million tons. The mine was closed in 1982 (Hakkou et al., 2008).

During its operation, more than 3 million tons of mine waste accumulated over an area of 16 hectares, without due consideration for environmental implications (Figure 2). The ore extracted from the Kettara mine contained various minerals, including pyrrhotite, sphalerite, galena, chalcopyrite, pyrite, arsenopyrite, and glaucodot. The main elements targeted for extraction were Cu, Fe, and S. Regrettably, the large quantities of waste materials, including tailings, were left untreated. Consequently, these materials were dispersed downslope by surface erosion and wind action, as well as through effluent drainage into lower-lying land used for the cultivation of paddy rice and household garden crops.

Notably, the abandoned Kettara mine is near two rural communities, known as Kettara Rural Center 1 and 2 (Figure 2), which together encompass approximately 7000 hectares, of which 72% is devoted to farmland. The region experiences a Mediterranean climate, bordering on arid and semi-arid conditions, with an average annual precipitation of 227 mm over a 10-year period. The temperatures exhibit significant daily and seasonal variations, with an average of 10.3°C in January and 37.2°C in July.

Figure 2. Geographic situation of Kettara rural communities KC1 and KC_2, and tailings ponds covering a large area in the Kettara region.

2.2. Sampling Description

To evaluate the spatial distribution of heavy metal contamination, 120 soil samples were systematically collected from agricultural lands within a 30-hectare area surroundingthe Kettara mine. Sampling points were spaced at regular 50-meter intervals, along a grid pattern to ensure homogeneous spatial coverage. At each point, soil was sampled from the 0–20 cm depth layer, after discarding the top 2 cm to eliminate surface contamination.

Each sample was collected with a clean garden shovel over a 100 cm² surface area and stored in pre-acid-washed polyethylene containers. Additionally, 6 background soil samples were collected 20 km upwind of the mining area, in an unaffected zone with similar soil characteristics, to serve as controls.

2.3. Soil samples analysis

The soil samples were collected from various sampling sites, including Kettara Rural Center 1 (KC_1), Kettara Rural Center 2 (KC_2), and Kettara mine tailings (KT). Each sample was collected at a depth of 0 to 0.2 meters, using a garden

shovel that had been thoroughly cleaned with concentrated nitric acid to eliminate any potential heavy-metal contaminants (Jung, 2001). Over 12 months, five samples were collected from each sampling site.

Soil samples were prepared for particle size distribution analysis by drying at 60°C for 75 hours, crushing, sieving (< 325 μm), homogenizing, and weighing. The hydrometer method was used to measure the soil particle size distribution.

To ensure accurate analysis, the soil samples were placed in pre-cleaned plastic containers that had been treated with concentrated nitric acid to prevent any trace of heavy metal contamination. Subsequently, the samples were dried and passed through a 2-mm sieve.

The pH of each sample was measured in a soil-water suspension (1:2.5, w/w), and electrical conductivity was measured in a 1:5 soil-to-water suspension utilizing an HI 9828 multiparameter portable instrument from HANNA Instruments (Badmus et al., 2014). The organic matter content was determined using the Walkley and Black procedure (Walkley and Black, 1934; Nelson and Sommers, 1982).

10 g of sieved sample was placed in a 500 ml wide-mouthed Erlenmeyer flask. To this, 10 ml of 1 N $K_2Cr_2O_7$ was added, and the flask was swirled gently to disperse the soil in the solution. 20 ml of Concentrated H_2SO_4 was then added slowly, followed by vigorous shaking for 1 min. Distilled water (200ml) was added to the flask, and the suspension was filtered. A few drops of ophenanthroline indicator were then added to the filtered solution and titrated against 0.5 N $FeSO_4$

H_2O. The sample without tailings was kept as a blank. The amount of organic carbon in the soil sample was calculated by using the following formula:

$$Organic\ content\ (\%) = \frac{(milliequivalents\ of\ K2Cr2O7\ -\ milliequivalents\ of\ FeSO4) \times 0.003 \times 100}{Masse\ of\ taillings\ sample}$$

% Organic Matter = % Organic Carbon 1.724.

Before analysis, the tailings samples were homogenized. Subsequently, these homogenized samples were stored in hermetically sealed polyethylene bags at 4°C until the commencement of the analysis (Barkouch et al., 2016; Wufem et al., 2013).

Aliquots of approximately 1 gram from each sample were digested with 5 mL of 65% HNO3 using a microwave digestion system to determine the HNO3-soluble fraction of heavy metals. The concentrations of Cd, Cu, Pb, and Zn were measured by a graphite furnace atomic absorption.

These comprehensive analytical procedures were conducted to obtain precise and reliable data on soil properties and heavy-metal concentrations, facilitating a thorough evaluation of the environmental impact of the Kettara mine and its surrounding areas.

3. Results and discussion

The textural characteristics of the soils under investigation are presented in Table 1, following the classification method by Shepard. The results revealed that coarse sand (2.0-1.0 mm) and fine sand (0.250-0.125 mm) were the dominant fractions in all agricultural soil samples, with a range from 25.6 to 21.2% and 26.0 to 23.0% in Kettara Center 1 (KC_1) and 2 (KC_2) soils, respectively.

Table 1. Average percentages grain-size (%) of different soils in Kettara region.

	KC_1	KC_2	MTK	Background soil
Clay	15.0 ± 3.1	18.6 ± 4.3	29.0 ± 3.0	15.5 ± 2.6
Fine silt	16.9 ± 2.8	20.0 ± 1.9	13.4 ± 2.6	19.5 ± 3.6
Coarse silt	11.0 ± 1.3	12.6 ± 2.0	13.7 ± 1.4	11.0 ± 1.2
Fine sand	26.0 ± 3.3	23.0 ± 3.5	19.8 ± 3.2	25.1 ± 0.6
Coarse sand	25.6 ± 3.4	21.2 ± 3.7	24.0 ± 2.9	25.0 ± 0.4

The geochemical soil characteristics, including pH, electrical conductivity (EC), and carbonate ($CaCO_3$) content, play a crucial role in understanding the soil's capacity to retain heavy metal pollutants (Barakat et al, 2022). Detailed numerical values for pH, EC, OM, OCC, $CaCO_3$, Cl^- and S^- for each sample are presented in Table 2.

The results of the soil pH measurements indicated that, overall, all sampled points exhibited slightly acidic to neutral pH levels, ranging from 6.7 to 6.9, which were lower than the background soil (7.7), except for the tailing sample, which displayed a very acidic pH of 5.2.

The observed variations in soil pH appeared to be influenced by the heterogeneous deposition of sulfuric

residues from mine tailings in the vicinity of the studied mine. The oxidation of these residues and the subsequent formation of sulfuric acid (approximately 0.9 to 1.3% of S^-) from these residues seemed to contribute to the decrease in pH, particularly in the tailing sample.

These findings suggest that mine tailings and associated sulfidic residues can affect soil pH, potentially influencing the soil's ability to retain heavy-metal pollutants. Such insights are critical for understanding the environmental implications of the Kettara mine and its surrounding areas and can aid in devising appropriate remediation strategies to address the potential risks posed by heavy metal contamination in the soil.

Table 2. Geochemical characteristics of different Kettara region soils

Parameters	KC_1	KC_2	MTK	Background soil
PH	6.7 ± 0.4	6.9 ± 0.4	5.1 ± 0.3	7.7 ± 0.3
E.C (μS/cm)	1706.2 ± 37.5	1830.4 ± 52.6	7569.7 ± 159.4	960.5 ± 81.9
OM (%)	4.6 ± 0.9	5.4 ± 0.8	3.3 ± 1.6	4.2 ± 0.9
OCC (%)	2.6 ± 0.5	3.3 ± 0.5	2.5 ± 0.9	2.9 ± 0.5
$CaCO_3$ (mg/g)	160.1 ± 29.2	120.9 ± 26.4	159.2 ± 19.4	129.8 ± 18.5
S %	1.3	0.9	4.1	0.3

The electrical conductivity (EC) exhibited greater variability than pH, with EC values ranging from 1706.2 to 1830.4 µS/cm. These values are significantly higher than those observed in background samples, indicating an increasing salinity gradient and high concentrations of labile ions near the mine area. The mine tailings area showed an exceptionally high EC value of 7569.7 µS/cm, primarily attributed to the elevated metal content in this region.

Particle size was found to be a significant factor influencing metal accumulation. Fine-grained soils showed higher nutrient concentrations due to their larger surface-to-volume ratio and enrichment in organic matter (OM) (Koiter et al., 2017).

The average organic matter content in the studied soils ranged from 4.6% in KC_1 to 5.4% dw in KC_2. This can be attributed to anthropogenic contributions, such as the discharge of domestic sewage in the Kettara region, which was an important source of organic matter in the mining zone. Additionally, agricultural activities in the vicinity of the mine contributed to the high organic content.

The organic carbon content (OCC) ranged from 2.6% dw in KC_1 to 3.3% dw in KC_2. OCC increased in KC_2 soils, corresponding to a decrease in soil grain size. The highest OCC was observed in soils with the lowest sand content and the highest silt and clay contents (Table 1).

Table 3 presents the estimated total concentrations (mg/kg) of heavy metals, namely Cd, Cu, Pb, and Zn, in the soils. The concentrations of these heavy metals were higher in KC_1 soils than in KC_2 soils. Local geology and anthropogenic influences were found to strongly determine the heavy metal concentrations in these soils.

Table 3. Mean concentrations of heavy metals in different Kettara region soils.

Metals	KC_1	KC_2	MTK	Background soil
Cd (mg/kg)	2.6 ± 0.7	2.2 ± 0.2	157.2 ± 8.8	0.4 ± 0.1
Cu (mg/kg)	427.8 ± 25.3	330.5 ± 22.8	969.1 ± 38.7	40.7 ± 0.7
Pb (mg/kg)	384.0 ± 27.1	355.3 ± 24.0	2640.7 ± 42.7	11.8 ± 1.4
Zn (mg/kg)	756,4 ± 74,3	690,5 ± 51,0	2846,8 ± 84,6	133,9 ± 2,0

Mineral weathering is a significant natural source of contamination, alongside various anthropogenic activities such as the use of fertilizers, herbicides, irrigation, and industrial effluents. In this agricultural region, the Kettara, abandoned mine tailings, are a prominent and likely major source of contamination.

Cu is widely distributed in aquatic ecosystems because it is a naturally occurring element. However, Cu and Zn concentrations are greatly influenced by anthropogenic sources.

Total Cu showed higher concentrations in CK_1 with 427.8 ± 25.3 mg/kg. Total Zn also showed similar trends with the highest level at the same soils with 756,4 ± 74,3 mg/kg. The results showed an increase in zinc in the soil due to domestic and industrial wastewater and agricultural runoff.

The results also showed significant spatial variations. Compared with the background soil, the concentrations of other heavy metals, in the studied soils showed a significant increase. The highest levels were observed in CK_1.

The calculated contamination factors (CF) (Table 4) indicate the extent of this increase in metallic contamination. The pollution index (PI) is the arithmetic mean of the CFs of the analyzed metals (Moghadam et al, 2024; Ferreira et al., 2022; Li et al., 2022; Boroujerdnia et al., 2020), and it allows an assessment of the degree of polymetallic pollution of the analyzed soil samples. A value greater than 1 indicates that the analyzed sample had a metallic contamination caused by human activities.

Table 4. Contamination factors (CFs) and pollution index (PI) of different Kettara region soils.

		Soil samples		
	Eléments	KC_1	KC_2	MTK
Contamination factors	Cd	6.5	5.5	393
	Cu	10.5	8.1	23.8
	Pb	32.5	30.1	223.8
	Zn	5.6	5.2	21.3
Pollution Index		**55.1**	**48.9**	**661.9**

The pollution index (Table 4) shows that the soils of CK_1 and CK_2 exhibit high levels of metal contamination, as their IP values significantly exceed the legal pollution limit of 1. Moreover, the respective IP values for CK_1 (55.1) and CK_2 (48.9) further indicate that these areas are highly polluted (Table 4).

Statistical comparisons between the two rural communities (KC1 and KC2) and the background soil show that differences in heavy metal concentrations are highly significant ($p < 0.05$), indicating a strong anthropogenic influence linked to historical mining activities. For example, cadmium levels in KC1 (2.6 mg/kg) and KC2 (2.2 mg/kg) are significantly elevated compared to the control soil (0.4 mg/kg), with similar trends observed for Cu (427.8 and 330.5 vs. 40.7 mg/kg), Pb (384.0 and 355.3 vs. 11.8 mg/kg), and Zn (756.4 and 690.5 vs. 133.9 mg/kg). These differences are further supported by contamination factors and pollution

indices, which confirm a high degree of soil enrichment in both villages. In addition, physicochemical parameters such as pH and electrical conductivity also show statistically significant deviations from the background soil. The pH in KC1 (6.7) and KC2 (6.9) is significantly lower than that of the control site (7.7), indicating increased acidity likely driven by sulfuric residues. Electrical conductivity values in KC1 (1706.2 µS/cm) and KC2 (1830.4 µS/cm) are approximately twice those of the control soil (960.5 µS/cm), indicating higher salinity and potential metal mobility. These statistically supported differences strengthen the interpretation that the elevated contamination in agricultural soils is not incidental but a direct consequence of proximity to the abandoned mine site.

Although no effective mitigation measures are currently at the Kettara site, several strategies could be considered to address heavy-metal contamination in soils. Potential remediation approaches include phytoremediation with tolerant plant species (Mahendra, 2024), soil washing techniques (Lianwen et al., 2018), and the use of stabilizing amendments such as lime or biochar to immobilize metals and improve soil pH (Lina et al., 2021). Additionally, policy interventions may include enforcing land-use regulations in contaminated areas, establishing long-term environmental monitoring programs, and developing rehabilitation plans for abandoned mining zones through coordinated efforts among governmental agencies, researchers, and local stakeholders. These general recommendations offer a framework for reducing environmental and health risks in affected regions.

4. Conclusion

The study demonstrated that soils in the Kettara rural communities exhibit altered physicochemical properties, with pH values ranging from 6.7 in KC1 to 6.9 in KC2, compared with 7.7 in the control soil. Electrical conductivity reached 1706.2 µS·cm^{-1} in KC1 and 1830.4 µS·cm^{-1} in KC2, notably higher than the control value of 960.5 µS·cm^{-1}. Sulfur contents were also elevated (1.3% in KC1 and 0.9% in KC2), reflecting the influence of mine tailings on soil acidification and metal mobility. Heavy-metal concentrations in KC1 reached 2.6 mg·kg^{-1} for Cd, 427.8 mg·kg^{-1} for Cu, 384.0 mg·kg^{-1} for Pb, and 756.4 mg·kg^{-1} for Zn, while in KC2 the respective values were 2.2, 330.5, 355.3, and 690.5 mg·kg^{-1}— substantially exceeding those in the background soil (0.4, 40.7, 11.8, and 133.9 mg·kg^{-1}). Contamination factors in KC1 ranged from 5.6 (Zn) to 32.5 (Pb), and in KC2 from 5.2 to 30.1, while pollution index values reached 55.1 and 48.9, respectively, confirming a high level of polymetallic contamination. These results clearly indicate that mining residues have significantly contributed to the degradation of agricultural soils in both communities, emphasizing the urgent need for targeted remediation and risk mitigation strategies.

Acknowledgments

Conflict of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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