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Sub-Threshold Ecotoxicological Risk of Zinc, Copper, and Cadmium in Soils Near Ceramic Industrial Zones: Implications for Agricultural Safety and Environmental Monitoring

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Abstract: Heavy metal contamination of soils near industrial zones is a globally recognized environmental threat, particularly as ceramic and allied manufacturing expands in low- and middle-income countries. This study investigates the spatial distribution and ecotoxicological risks of zinc (Zn), copper (Cu), and cadmium (Cd) in surface soils surrounding a ceramic production facility. Eleven soil samples (0–10 cm depth) were analyzed using Atomic Absorption Spectrophotometry (AAS). Zinc, copper, and cadmium concentrations ranged from 0.56–2.89 mg/kg, 0.09–2.07 mg/kg, and 0.007–0.058 mg/kg, respectively, all below WHO/FAO permissible limits for agricultural soils. Despite these sub-threshold values, the presence of bioavailable cadmium, a persistent, non-essential element—raises significant concerns for long-term ecological integrity and food safety. The spatial gradient of metal accumulation, with higher concentrations nearer to the factory and decreasing outward, supports the identification of point-source pollution from industrial activity. The study emphasizes the importance of re-evaluating regulatory thresholds in light of chronic, low-dose exposure and highlights AAS as a cost-effective, globally deployable monitoring method in data-scarce regions. This research contributes novel insight into the environmental footprint of ceramic manufacturing, an underexamined sector, and presents a reproducible model for metal risk assessment applicable across industrializing regions worldwide.

1. Introduction

Industrial development has emerged as a double-edged sword in the global sustainability discourse. While it enables economic growth and infrastructure expansion, manufacturing processes, especially in unregulated or semi-formal settings have increasingly contributed to the degradation of soil quality. Among the most persistent pollutants are heavy metals such as zinc (Zn), copper (Cu), and cadmium (Cd), which are known for their non-biodegradable nature, potential for bioaccumulation, and ecotoxicological impacts on terrestrial ecosystems and food chains (Wuana and

Okieimen, 2011; Alloway, 2013; Karim *et al.*, 2016 & 2019). While considerable research has focused on emissions from mining, metal smelting, and tanneries, ceramic manufacturing has received relatively little attention as a source of trace metal pollution. Yet, this industry frequently utilizes raw materials such as kaolin, feldspar, quartz, and various glazes that contain metal oxides, especially of Zn and Cu. These inputs, coupled with inadequate waste management practices, can lead to the direct or fugitive release of metals into nearby soils through effluents, emissions, and solid waste (Amiri *et al.*, 2021; Emurotu and Azike, 2022).

Over time, even low-level emissions can accumulate in surface soils, leading to ecological disruption and potential public health risks, particularly in agricultural communities surrounding industrial zones. Cadmium, a non-essential and highly toxic metal, is of particular concern due to its strong soil mobility and tendency to accumulate in edible plant tissues. Chronic human exposure to cadmium has been linked to renal dysfunction, bone demineralization, and carcinogenic effects (ATSDR, 2007). Copper and zinc, while essential micronutrients, may become phytotoxic at elevated concentrations, disrupting enzymatic activity, nutrient uptake, and soil microbial function (Alloway, 2013; Opaluwa *et al.*, 2012).

These risks are exacerbated in tropical and sub-Saharan environments, where soils are typically sandy, acidic, and low in organic matter, conditions that enhance metal solubility and plant uptake (Olatunji and Osibanjo, 2014; Oteno *et al.*, 2023). Moreover, environmental monitoring programs in such regions are often underfunded, leaving substantial knowledge gaps regarding contamination sources and long-term ecological consequences. Various plants served to absorb heavy metals (El-Sappah *et al.*, 2024), such as *Luffa Cylindrica* (Ad *et al.*, 2015), Indian mustard (Brassica juncea L.) (Farooq *et al.*, 2022; Bd *et al.*, 2015).

This study addresses these gaps by investigating the concentrations and ecological risk potential of Zn, Cu, and Cd in soils surrounding a ceramic manufacturing zone. The specific objectives are to:

1. Assess the concentrations and spatial gradients of Zn, Cu, and Cd in surface soils near a ceramic industrial facility;
2. Evaluate the ecotoxicological implications of sub-threshold metal concentrations based on WHO/FAO soil guidelines;
3. Propose a transferable monitoring framework for low-resource settings using Atomic Absorption Spectrophotometry (AAS) as a practical and cost-effective analytical tool.

2. Materials and Methods

2.1 Study Area Description

The study was conducted around an industrial ceramic manufacturing facility located in a semi-urban region with agricultural activity. The surrounding area is characterized by tropical conditions, with moderate-to-high rainfall and seasonal farming practices. Soils in the area are typically loamy-sandy, moderately acidic, and exposed to airborne emissions and water runoff from the factory site.

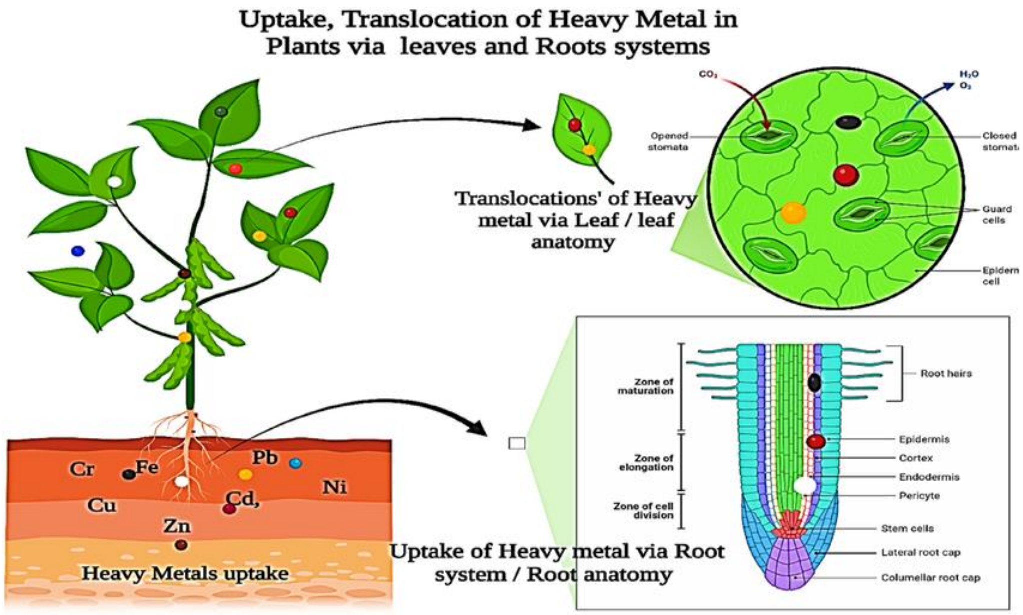

Fig 1. Schematic diagram illustrating the uptake, translocation, and sequestration of heavy metals (Zn, Cu, Cd) in plants — via roots, stems, and leaves

2.2 Soil Sampling

Eleven surface soil samples (0–10 cm depth) were collected within an 80-meter radius from the factory's perimeter. Sampling points were chosen to reflect proximity gradients from suspected emission zones, with 10–15 m spacing between sites. Soil was collected using stainless-steel trowels and placed into labeled polyethylene bags to prevent cross-contamination.

2.3 Sample Preparation and Digestion

Soils were air-dried, sieved through a 2 mm mesh, and homogenized. For digestion, 2 g of each sample was treated with 20 mL of freshly prepared aqua regia (3:1 $HCl:HNO_3$) following USEPA Method 3050B. The mixture was heated at 95°C for 2 hours, filtered, and diluted to 50 mL with deionized water.

2.4 Metal Analysis via Atomic Absorption Spectrophotometry (AAS)

Metal concentrations were measured using Atomic Absorption Spectrophotometry (Model AA500, PG Instruments, UK). Wavelengths used were 213.9 nm for Zn, 324.8 nm for Cu, and 228.8 nm for Cd. All analyses were performed in triplicate with appropriate blanks and calibration standard as shown in Table 1.

2.5 Quality Control

Procedural blanks, replicate samples, and calibration verification standards were included in each batch. All reagents were of analytical grade, and glassware was acid-washed. AAS calibration curves showed $R^2 > 0.995$ for all metals.

Table 1. Analytical Wavelengths Used for Atomic Absorption Spectrophotometric Determination of Selected Heavy Metals

Metal	Wavelength (nm)
Zinc (Zn)	213.9
Copper (Cu)	324.8
Cadmium (Cd)	228.8

3. Results

3.1 Metal Concentration Profiles

Table 2 and Figure 2 present concentrations of Zn, Cu, and Cd in the eleven soil samples. Zn ranged from 0.56–2.89 mg/kg, Cu from 0.09–2.07 mg/kg, and Cd from 0.007–0.058 mg/kg. The highest values for all metals were observed at points closest to the factory, suggesting localized industrial input. Despite being below WHO/FAO limits (Zn = 50 mg/kg, Cu = 36 mg/kg, Cd = 0.8 mg/kg), the persistence and distribution pattern of Cd, in particular, are notable for long-term ecological risk.

Table 2. Heavy Metal Concentrations in Soil Samples Near a Ceramic Industrial Zone

Sample ID	Zn (mg/kg)	Cu (mg/kg)	Cd (mg/kg)
S1	2.886	2.072	0.018
S2	1.456	1.116	0.037
S3	1.822	0.708	0.049
S4	1.300	0.266	0.037
S5	1.212	0.251	0.050
S6	0.955	0.231	0.050
S7	2.010	0.228	0.030
S8	2.088	0.978	0.009
S9	0.555	0.086	0.058
S10	1.461	0.165	0.043
S11	1.158	0.215	0.007

- **Interpretation Notes**:

CF > 1 indicates contamination above background levels.
I_geo > 0 suggests pollution from anthropogenic sources.
Samples S1–S10 show elevated cadmium with *I_geo(Cd)* > 1 in many cases, indicating real ecological concern even when absolute concentrations are "low."

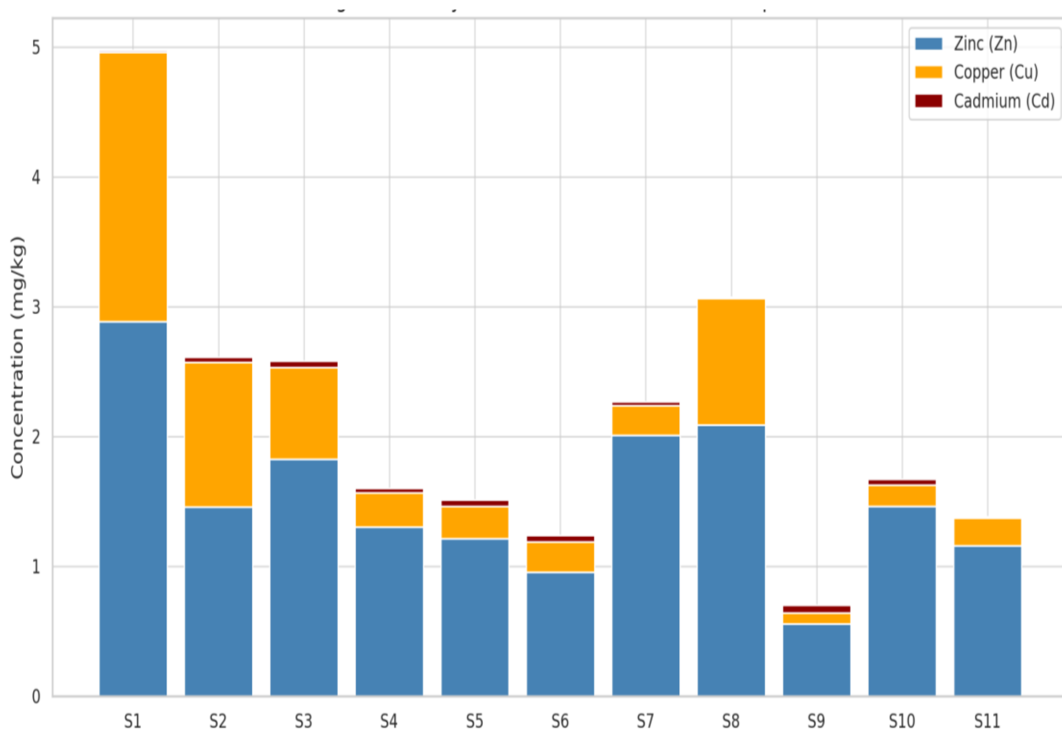

Fig 2. Heavy Metal Concentration in Soil Samples

4. Discussion

4.1 Spatial Distribution and Industrial Influence

The results indicate measurable concentrations of zinc (Zn), copper (Cu), and cadmium (Cd) in all sampled soils, with notably higher values at locations closest to the ceramic production facility. This spatial gradient supports the hypothesis of point-source contamination linked to industrial activities, a pattern consistent with previous studies on localized heavy metal enrichment around manufacturing zones. Although all measured concentrations remained below WHO/FAO permissible thresholds (Table 3), their detection across all samples reflects persistent environmental loading. Cadmium, in particular, raises ecological concern due to its high mobility and long-term toxicity. The contamination factor (CF) and geoaccumulation index (I_geo) values (Table 4, Fig. 3 and 4) further substantiate these concerns, with many samples exceeding natural background levels despite sub-threshold concentrations.

Table 3. WHO/FAO Limits and Observed Metal Ranges in Soil

Metal	Observed (mg/kg)	Range WHO/FAO (mg/kg)	Limit % Samples Above 50% of Limit
Zinc (Zn)	0.56 – 2.89	50	0%
Copper (Cu)	0.09 – 2.07	36	0%
Cadmium (Cd)	0.007 – 0.058	0.8	0%

Table 4. Contamination Factor (CF) and Geoaccumulation Index (I_geo)

Sample ID	CF_Zn	CF_Cu	CF_Cd	I_geo_Zn	I_geo_Cu	I_geo_Cd
S1	5.77	6.91	1.85	1.944	2.203	0.303
S2	2.91	3.72	3.73	0.957	1.311	1.314
S3	3.64	2.36	4.94	1.281	0.654	1.720
S4	2.60	0.89	3.70	0.793	-0.758	1.303
S5	2.42	0.84	4.98	0.692	-0.842	1.731
S6	1.91	0.77	5.05	0.349	-0.963	1.751
S7	4.02	0.76	2.95	1.422	-0.983	0.976
S8	4.18	3.26	0.92	1.477	1.119	-0.705
S9	1.11	0.29	5.76	-0.434	-2.379	1.941
S10	2.92	0.55	4.34	0.962	-1.452	1.533
S11	2.32	0.72	0.71	0.627	-1.068	-1.079

4.2 Ecotoxicological Implications and Soil–Plant Transfer

The ecological risk of heavy metals is not solely defined by their absolute concentrations, but also by their bioavailability and tendency to accumulate in biotic systems. As shown in Figures 5 and 6, the average proportional composition reveals cadmium's smaller mass share relative to Zn and Cu, yet it consistently exhibited the highest CF and I_geo values—demonstrating that even low-level contamination can be toxicologically relevant.

Once released into the soil, Zn^{2+}, Cu^{2+}, and Cd^{2+} ions can be absorbed by plant roots, translocated to shoots, and deposited in edible tissues (Figure 7). Numerous studies have shown cadmium's preferential accumulation in leafy vegetables and tuber crops, with minimal physiological barriers. This represents a critical pathway for human and animal exposure, particularly in communities reliant on subsistence farming near industrial areas.

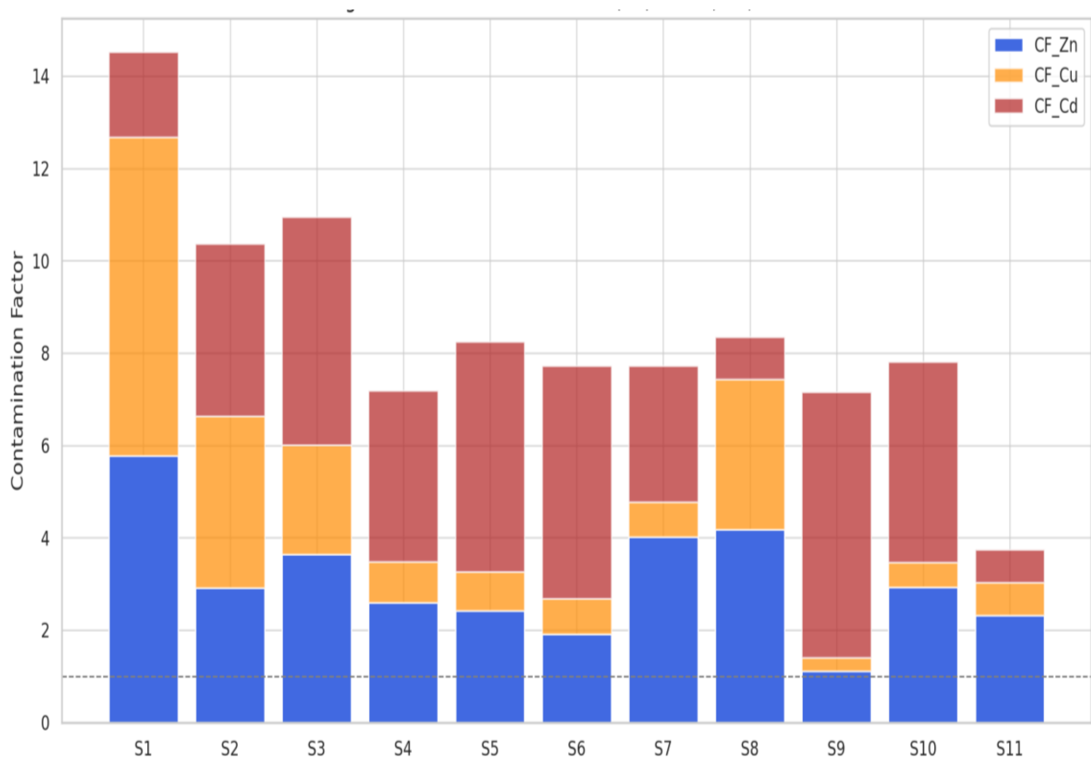

Fig 3. Contamination Factor (CF) for Zn, Cu, and Cd

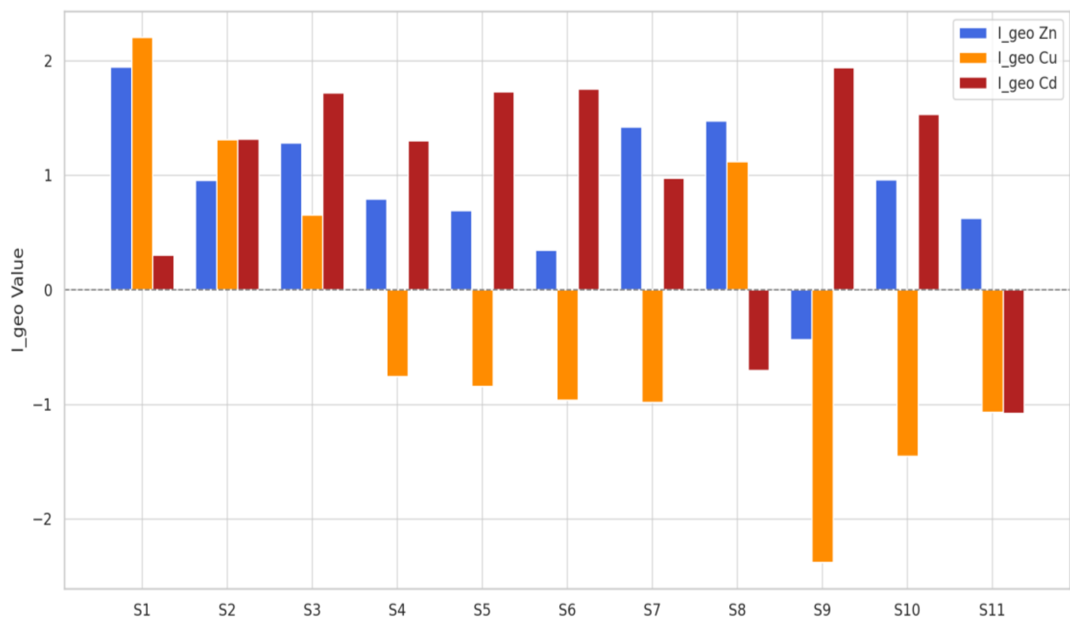

Fig. 4. Geo-accumulation Index (I_geo) for Zn, Cu, and Cd

As illustrated in Figure 8, the uptake of these metals can cause a range of toxicological effects at the molecular and cellular levels, including membrane damage, chlorosis, reduced enzymatic activity, and inhibition of photosynthesis. Microbial disruption in the rhizosphere may also lead to long-term soil degradation and compromised fertility, even in the absence of visible crop symptoms.

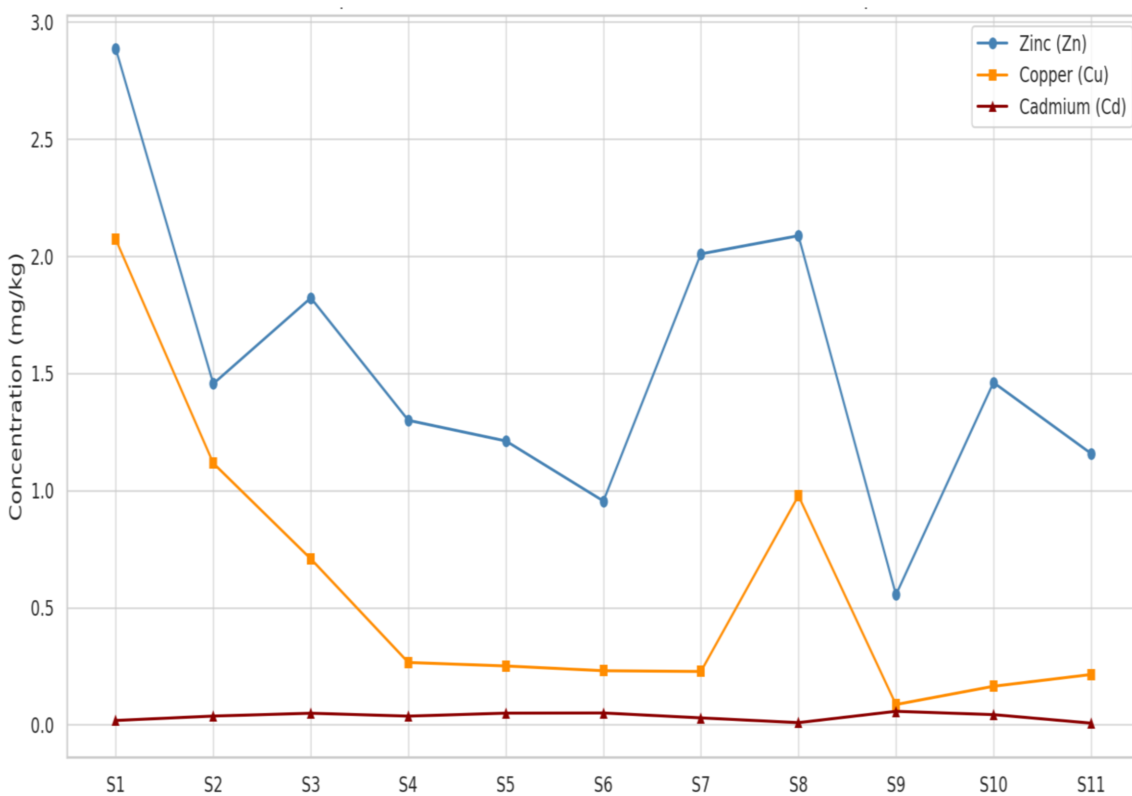

Fig 5. Graphical Representation of Variation of Metal Concentration Across Soil Samples

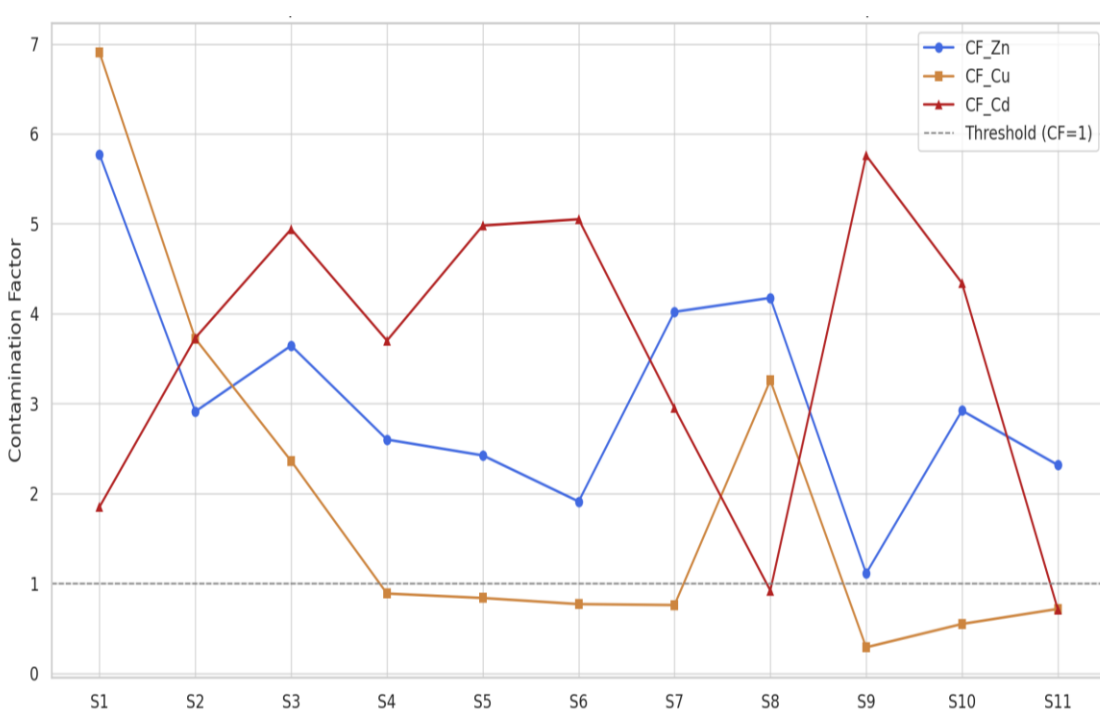

Fig 6. Graphical Representation of Contamination Factor, (CF) of Zn, Cu, and Cd Across Samples

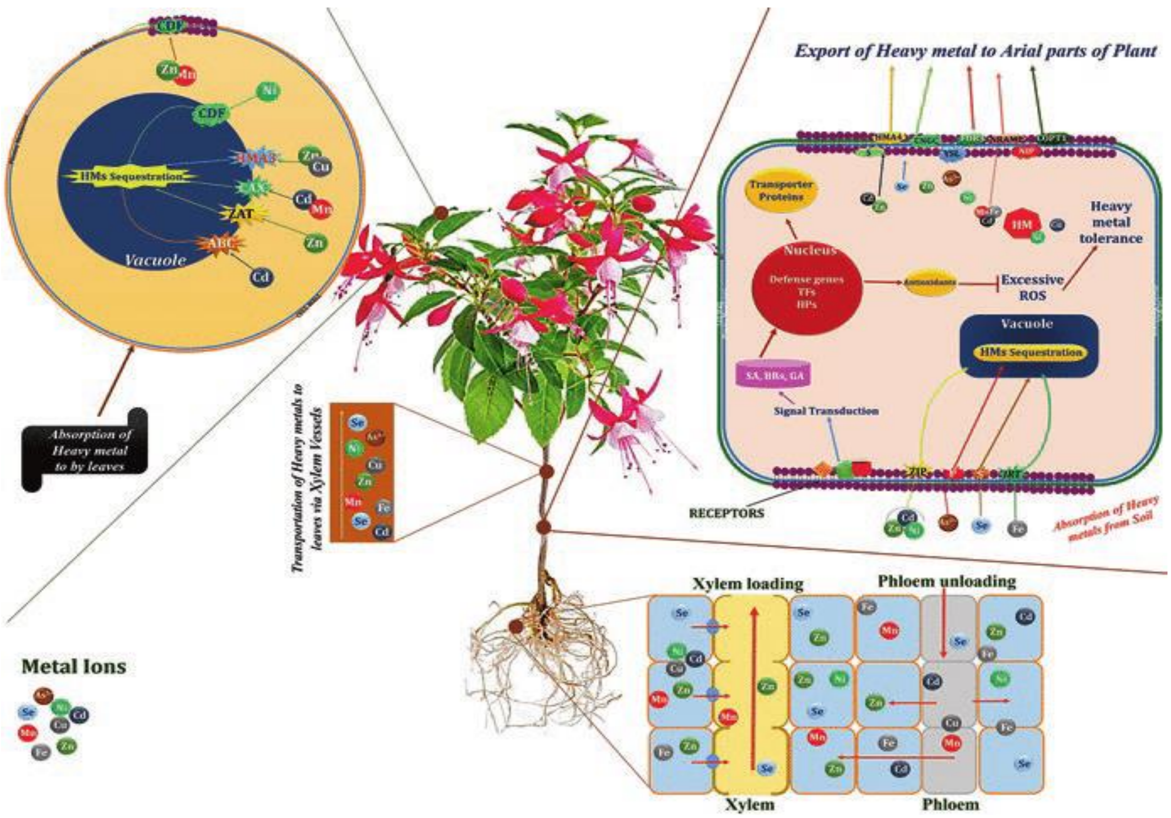

Fig 7. Illustration of uptake mechanisms within plant root cells, showing signaling pathways and cellular organelle stress responses to metal exposure.

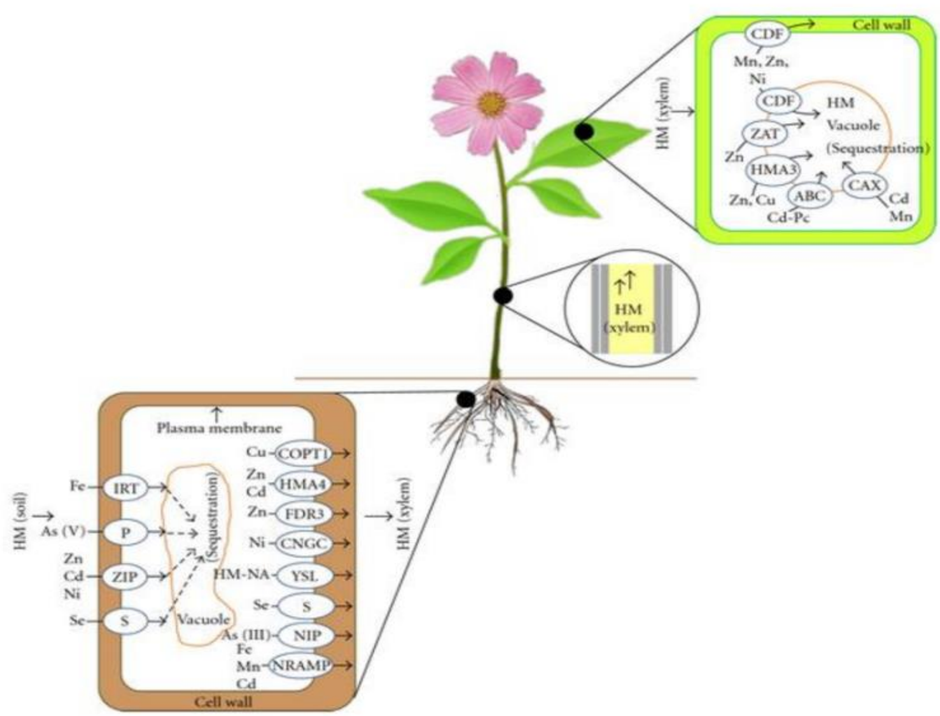

Fig 8. Diagram showing both direct and indirect toxic effects of heavy metals on crop plants, including reduced growth and microbial disruption.

4.3 Comparative Literature Context

The observed trends in this study align with those of Emurotu and Azike (2022), who documented Cd and Cu accumulation in food crops near a ceramic facility. Similar spatial contamination profiles were reported in Ajaokuta's steel belt (Olatunji and Osibanjo, 2014; Oteno *et al.*, 2023), reinforcing the notion that underregulated industrial operations including ceramics contribute substantially to localized soil pollution. However, unlike metallurgy or mining, ceramic manufacturing remains **underrepresented** in global contamination assessments.

4.4 Analytical Relevance of AAS in Industrial Monitoring

The use of Atomic Absorption Spectrophotometry (AAS) proved reliable and practical for trace-level detection of Zn, Cu, and Cd in soil. While techniques like ICP-MS offer superior sensitivity, AAS remains highly appropriate for routine environmental assessments in low-resource settings, offering a cost-effective, scalable, and technically accessible method. This is particularly relevant in developing economies experiencing rapid industrialization without commensurate environmental oversight.

4.5 Novelty and Global Implications

This study contributes novel insights into the ecotoxicological risk of heavy metals from ceramic industries, a sector not commonly associated with soil contamination in the global literature. It challenges the assumption that regulatory compliance (i.e., being "under the limit") equates to environmental safety. The notion of "silent contamination" sub-threshold pollution with significant biological effects demands a reconsideration of current risk thresholds and monitoring strategies.

The findings have broad relevance, particularly for emerging economies, where industrial expansion often outpaces environmental regulation. This underscores the need for:

1. Updated soil metal guidelines considering chronic low-dose exposure,
2. Expansion of monitoring programs to include underrepresented industries,
3. and integration of ecological indicators beyond concentration-based thresholds.

5. Conclusion and Recommendations

This study demonstrates that ceramic manufacturing facilities can serve as point sources for trace metal contamination in adjacent soils. Although detected concentrations of Zn, Cu, and Cd were within permissible limits, their presence especially cadmium presents long-term ecotoxicological and food safety concerns (Fig. 9).

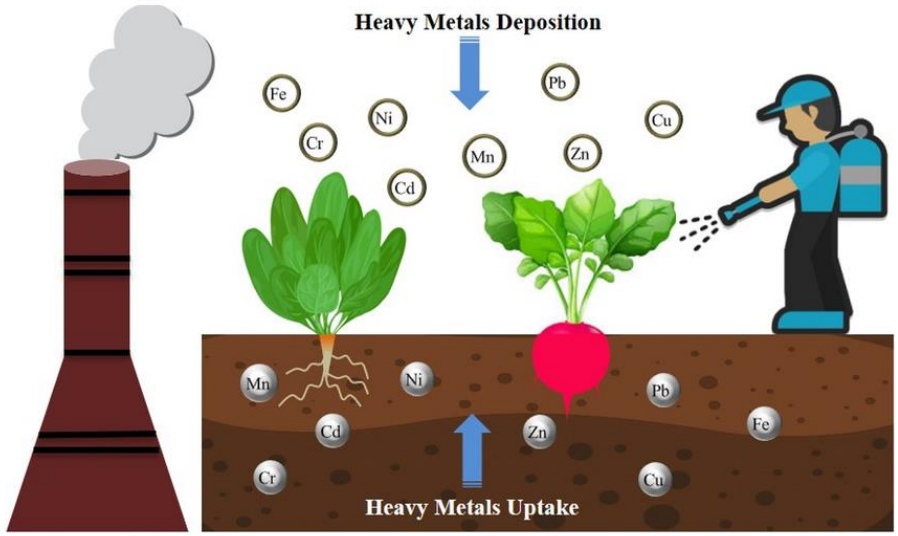

Fig 9. *Conceptual schematic diagram of metal deposition in root and leafy vegetables through soil-to-plant transfer*

Recommendations:

1) Regular soil monitoring using cost-effective methods like AAS;
2) Review of global regulatory thresholds to consider chronic exposure effects;
3) Implementation of vegetative buffer zones and industrial containment strategies;
4) Promotion of phytoremediation and organic amendments in contaminated areas;
5) Global recognition of emerging pollution sources, including ceramics and informal manufacturing.

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Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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