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Understanding Heavy Metal Contamination in Soil: A Comprehensive Risk Assessment

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ABSTRACT

Urban soil contamination by heavy metals poses a significant environmental and public health challenge. As an assessment of four heavy metals in urban soils of Hyderabad, Pakistan, employing spatial variability mapping, geographic information system (GIS), and multivariate analysis. A total of 415 soil samples were collected from different urban areas, processed, and analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The results revealed distinct groups of elements, with Cd, Pb, and Zn displaying anthropogenic origins, while as showed natural abundance. GIS-based maps identified metal contamination hotspots, with Zn and Pb concentrations elevated in the city center, primarily attributed to vehicular emissions. The study also highlighted Ni hotspots in industrial areas and the Phulleli canal. The potential ecological risk (PER) assessment indicated moderate and considerable risk only for Cd. Integrated PER analysis revealed that 95% of samples had low PER, emphasizing the importance of these findings for guiding future urban planning and research and development activities. This comprehensive assessment provides valuable insights for policymakers,government authorities, and stakeholders to address and mitigate heavy metal contamination in urban soils.

KEYWORDS

Soil pollution - Heavy Metal contamination - Impact - Urban soil – Soil pathways

1. LITERATURE REVIEW

Soil pollution is a critical issue caused by various pollutants such as heavy metals. These pollutants are introduced through sewage, waste, accidental discharge, and industrial and agricultural chemicals. The main cause of soil pollution is heavy metals accumulation. It disruptssoil fertility and general functioning. Heavy metals are ubiquitous in the earth's environment andcan result from both anthropogenic and natural activities. Industrialization, urbanization and intensified agriculture are the main causes of heavy metal contamination of soils and the environment. Heavy metals are elements with metallic properties, a density of >5 g cm^{-3} and an atomic mass of >20. The most common heavy metals in the environment are **As, Pb, Zn and Cd.** Thus, the excess of such heavy metals is a threat to the environment. It is crucial to-

-understand the pollution characteristics of these contaminated sites and implement remedial treatments to preserve soil fertility and productivity. [1]

Urban soils, influenced by anthropogenic activities, interact with diverse pollutants, especially heavy metals entering the human body through skin contact, ingestion, and inhalation. Identifying potentially toxic elements is crucial for resident safety and policymakers' attention. Physical and chemical methods have been used for remediating heavy metal contaminated soil, but physical and chemical approaches have limitations like high costs, substantial energy requirements, and the potential for secondary pollution therefore, advanced analytical techniques, such as geostatistical approaches like ArcGIS®, help assess human-driven or natural sources' impact on soil heavy metal accumulation. Toxic elements in soil raise concerns for geochemical studies, prompting scientific risk assessments. Geochemical mapping, widely regarded for presenting spatial element concentrations, aids in assessing soil quality globally.

The environmental and human health consequences of heavy metals depend on how each metal moves through environmental compartments and the pathways by which they reach humans and the ecosystem. The concerning pollution status of heavy metals in Pakistan is emphasized by numerous conducted studies, indicating the severity of the issue, the further research assesses the risk assessment related to such heavy metal accumulation. [2]

2. SOURCES AND HARMFULNESS OF HEAVY METALS

2.1.1 FROM ATMOSPHERE TO SOIL DEPOSITS

Heavy metals from energy production, transportation, metallurgy, and construction enter the atmosphere as aerosols and deposit into soil naturally. Lead pollution in Central Sweden was linked to emissions from urban industrial sources.[3]. Heavy metals from various industries enter the atmosphere as aerosols and deposit them into soil naturally. Lead pollution in CentralSweden was linked to emissions from urban industrial sources like a copper plant and mining waste.[4]. A sulfuric acid plant in Russia impacted the environment with chromium, cadmium, and arsenic emissions from its chimneys. [5]

Table 1. Different sources of heavy metals contaminating soils annually in the world [6]

Sources	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Agriculture and Food Waste	0-0.6	0-0.3	4.5-9.0	3-38	0-1.5	6-45	1.5-27	12-150
Farmyard Manure	1.2-4.4	0.2-1.2	10-60	14-80	0-0.2	3-36	3.2-20	150-320
Logging and Timber Industry Waste	0-3.3	0-2.2	2.2-18	3.3-52	0-2.2	2.2-23	6.6-8.2	13-65
Municipal Wastes	0.09-0.7	0.88-7.5	6.6-33	13-40	0-0.26	2.2-10	18-62	22.97
Municipal Sludge	0.01-0.24	0.02-0.34	1.4-1.1	4.9-21	0.01-0.8	5.0-22	2.8-9.7	18-57
Organic Wastes	0-0.25	0-0.01	0.1-0.48	0.04-0.61	-	0.17-3.2	0.02-1.6	0.13-2.1
Metal Processing and Coal Ash	0.01-0.21	0-0.08	0.65-2.4	0.95-7.6	0-0.08	0.84-2.5	4.1-11	2.7-19
Fertilizer	6.7-37	1.5-13	149-446	93-335	0.37-4.8	56-279	45-242	112-484
Marl	0-0.02	0.03-0.25	0.03-0.38	0.05-0.58	-	0.20-3.5	0.42-2.3	0.25-1.1
Commodity Impurities	0.04-0.5	0-0.11	0.04-0.19	0.15-2.0	0-0.02	0.22-3.5	0.4-2.6	0.15-3.5
Solid Wastes	31-41	0.78-1.6	305-610	395-790	0.55-0.82	6.5-32	195-390	310-620
Total	52-112	5.6-38	484-1309	541-1367	1.6-15	106-544	479-1113	689-2054

2.1.2 SEWAGE SLUDGE SEEPAGE INTO SOIL

Heavy metals like Hg, Cd, Pb, Cr, etc., enter the soil through irrigative sewage and accumulate over time. Although sewage irrigation is a feasible solution for crop irrigation in aridareas, the risk of heavy metal contamination requires strict control of irrigative sewage quality tocomply with national irrigation water standards. [6]

2.1.3 SOLID WASTE LEACHING IN GROUND

Mining and industrial waste contain heavy metals that can contaminate water and soil. In China, over 80 sewage treatment plants generate 400 million tons of sludge with high organic matter, nitrogen, and phosphorus content.[7] Sludge application to soils for treatment often leads to exceedances of control standards for Cr, Pb, Cu, Zn, and As. Wind and water facilitate theeasy expansion of the contamination scope of solid wastes. [8]

2.1.4 AGRICULTURE SUPPLIES TO SOIL PATHWAYS

Phosphoric fertilizers are a major source of toxic heavy metals in fertilizers. The heavy metal content in compound fertilizers follows the sequence of phosphoric fertilizer > compound fertilizer > potash fertilizer > nitrogen fertilizer. [9]. Cadmium (Cd) is introduced throughphosphoric fertilizers, leading to increased soil Cd levels and plant uptake. [10] The widespread adoption of mulch in recent years has led to "white pollution" in soils due to the inclusion of heatstabilizers containing Cd and Pb during mulch production, further contributing to heavy metal contamination of soils. [11]

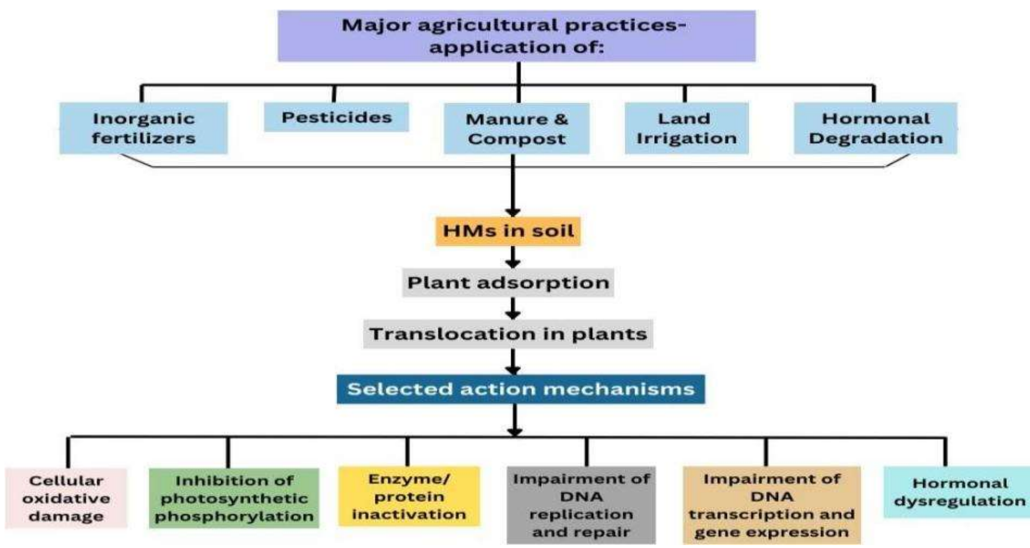

Figure 1. A flow chart showing the contamination of HM using agricultural practices [11]

3. IMPACT OF HEAVY METAL CONTAMINATION OF SOILS

Microbial biomass serves as an important indicator of soil contamination extent, with severe inhibition observed in heavy metal-contaminated soil. Enzyme activities are substantially reduced with increasing heavy metal concentrations [12] Heavy metals in soil, especially Cd, harm plant growth by inhibiting root length, decreasing plant height, and leaf area. [10] Heavy metals in urban soils can harm humans, especially children, through skin absorption and inhalation. Excess intake of essential metals such as Cu, Zn, and Ni can also be harmful to human health.[13]

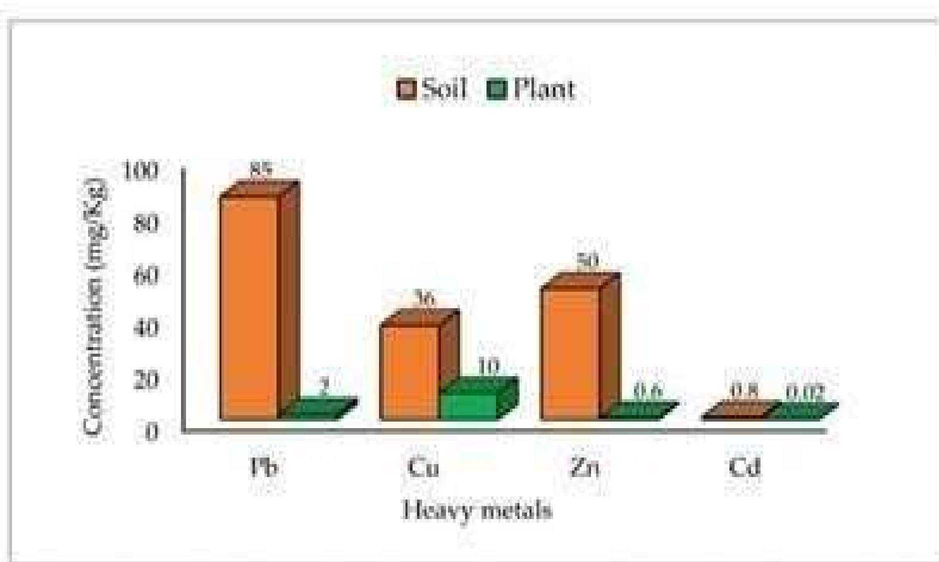

Figure 2. *Permissible limits for concentrations of heavy metals in the soil and plants (Modified after WHO)* ***[14].***

4. RISK ASSESSMENT

4.1.1 STUDY AREA AND SOIL SAMPLING TECHNIQUES

The study area is **Hyderabad**, situated on the **East Bank** of the **River Indus**, spanning a total area of 237 square kilometers, known for its moderate climate. In May 2022, amid a temperature of around 41ºC, 415 surface soil samples (1–25 cm deep) were collected in the Hyderabad district. The sampling employed a 1 × 1 km grid in densely populated and industrial areas. For buildings and road sites, a 2 × 2 km grid was used. Each sampling site yielded 1.5 kgof soil, sieved to a 2 mm fraction. Digestion of samples was carried out using combination of HNO_3-$HClO_4$-HCl of Analytical Grade in a Teflon digestion vessel, and the metal (Cd, Ni, Zn, As,) concentration was determined.

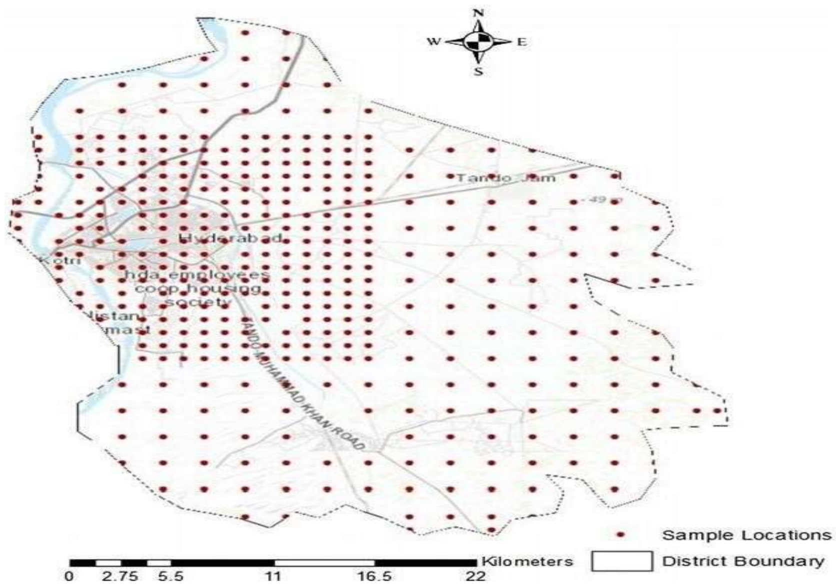

Figure 3. *Sampling sites in district Hyderabad, Pakistan*

4.1.2 POTENTIAL ECOLOGICAL RISK ASSESSMENT

To comprehensively assess metal pollution, the study calculated the Pollution Load Index(PER) from representative soil samples using a validated quantitative approach recommended byprior studies.

$$CF = Cn\,(3)\frac{sample}{Cn(Crust)} \qquad (3)$$

$$ER = Tr \times CF \tag{4}$$

$$RI = (5)\, Er \tag{5}$$

Where, RI is the integrated PER index of harmful metals, Er is PER index for one element, Tr is the factor for toxic response of metals, Cn is background concentration of specific metal and Cr is the factor of pollution for specific metal. The urban soil of the Hyderabad district was analyzed for the concentrations of four selected metals namely Cd, Zn, Pb and As. The pollution index that of Pb, Cd and As exhibited significant concentration ranges. Cd from **0.91** to **13.4 mg kg^{-1},** and Pb from **7.3** to **76.4 mg kg^{-1}.** Median values for Zn and Cd were notably lower than their mean values indicating a skewed distribution, while high values of Relative Standard Deviation (RSD) indicate accumulation of anthropogenic influences in urban soil.

Table 2. Concentration (mg kg^{-1}) of metals in urban soil of Hyderabad, Pakistan

	Cd	Zn	Pb	As
Mean	3.9	115.2	26.2	2.3
Median	3.0	114.2	26.3	2.3
Min	0.9	104.2	7.3	1.3
Max	13.4	125.1	76.4	3.1
Range	12.4	20.9	69.1	1.8
RSD	53.7	3.20	47.1	12.5
PI	1.390	0.999	1.135	1.004
P (S-W) Test	0.000	0.195	0.000	0.068
World Soils	0.35	90.0	35.0	6.0

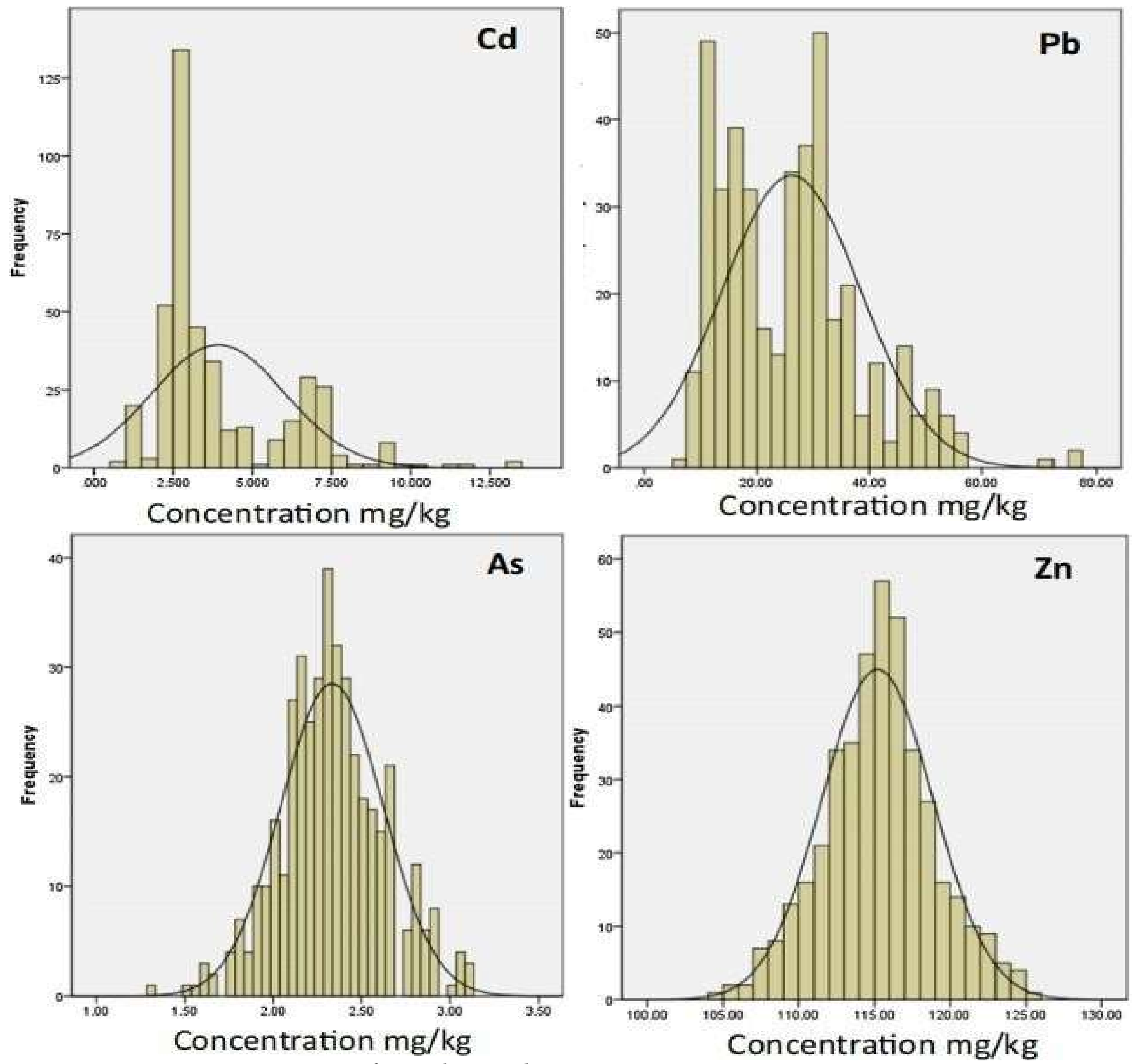

Figure 4. Frequency Histograms of metals in urban district Hyderabad, Pakistan

4.1.3 MAPPING AND SPATIAL ANALYSIS

The metals, distributed across space, increased concentrations of **Cd, Pb**, and **Zn** were noted in densely populated and industrial sections of the city, with lower concentrations observedaround the city center. Meanwhile, the distribution of **As** in the soil of Hyderabad district appeared to be random. It has been noted that **Zinc (Zn)** accumulates in urban soils due to traffic emissions, particularly from vehicle tires. It was noted that the highest Zn concentration was **125.1 mg/kg**. **Pb** concentration was observed near the Phulleli canal city center where it receives municipal waste from various human activities and industrial areas, also displayed noteworthy **Pb** concentrations.

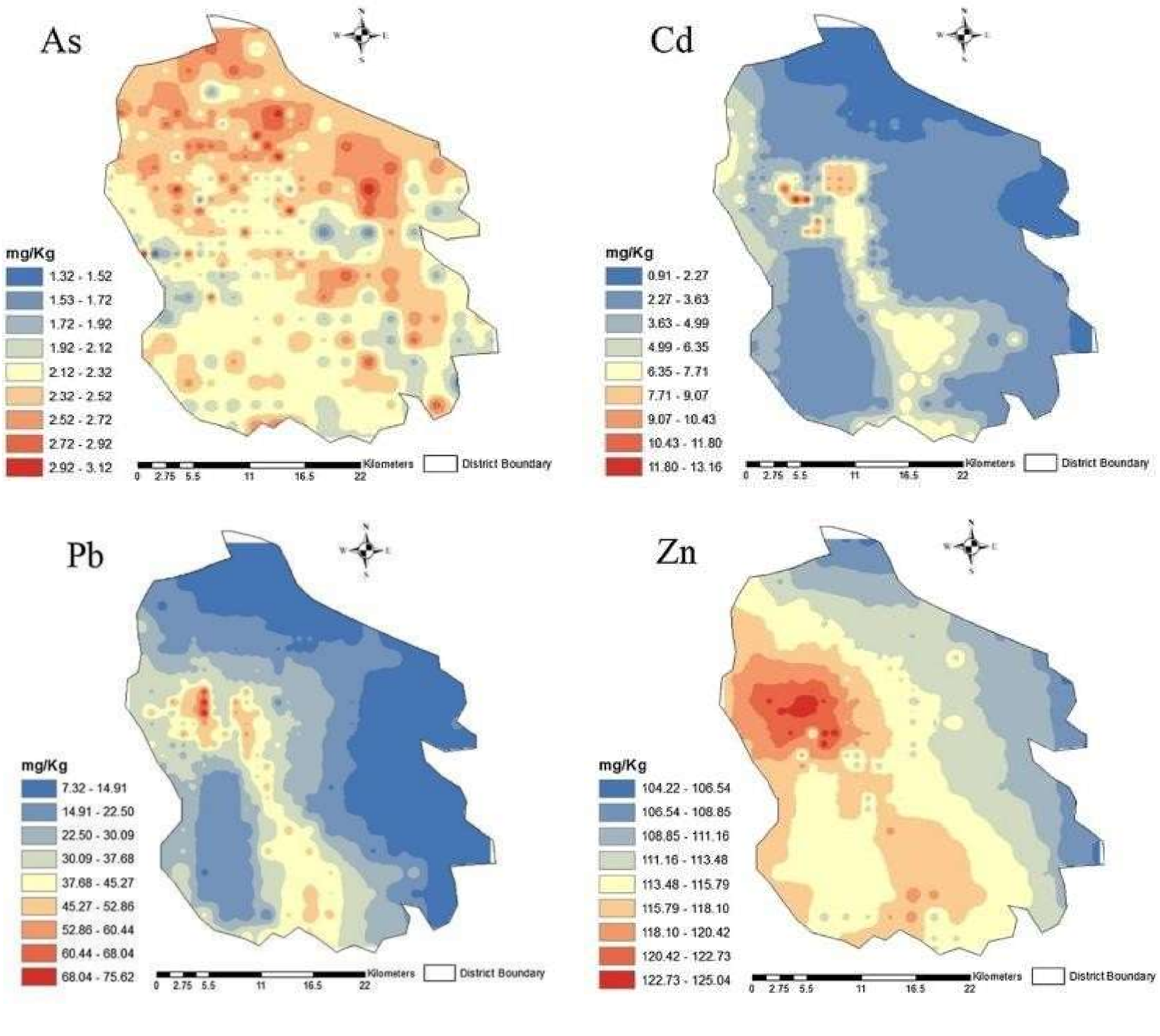

Figure 5. Spatial Distribution of concentrations of heavy metals in urban soils in district Hyderabad, Pakistan

Table 3. Levels of potential ecological risk and risk grades indexes of toxic elements pollution (Hakanson, 2020).

E^r	RI (Risk Index)	Potential Ecological Risk Grade
< 40	< 150	Low
40 – 80	150-300	Moderate
80 - 160	300-600	Considerable
160 - 320	-	High
<320	> 600	Very High

Table 4. Potential ecological risk index of single element (E_r) and integrated Risk Index (RI).

Statistics	Elements				RI
	As (Er)	Pb (Er)	Cd (Er)	Zn (Er)	
Mean	10.05	5.65	41.71	1.00	70.40
Maximum	13.49	16.49	142.09	1.09	187.82
Minimum	5.05	1.58	9.68	1.99	31.99

The comprehensive potential ecological risk (PER) assessment revealed that in 95% of the samples, the combined Risk Index (RI) for elements As, Cd, Pb, and Zn was below 150, indicating a low potential ecological risk. However, 5% of the samples had an RI between 151 and 185, representing a moderate potential ecological risk. This suggests that human activities are significantly contributing to environmental contamination, posing a threat to the ecosystem. Without effective control measures, there is a risk of escalating to considerable and high potential ecological risks.

5. CONCLUSION

Four different heavy metals were studied in the district Hyderabad, Pakistan, Metals **Cd, Pb**, and **Zn** were in higher concentration in city centre, as against other adjoining areas of the Hyderabad city. Whereas the concentrations of **As** specifically was found random or in irregular pattern, representing its natural source of origin. After the mapping and spatial analysis of single element concentration was observed in the district Hyderabad, upon formulation Single Element Ecological Risk of elements was observed. **Cd** was observed 142.09 (maximum) which is considerable according to (Hakanson, 2020), while RI of elements **As, Cd, Pb** and **Zn** was 187.82 which represented the moderate Potential Ecological Risk Index. The results from the descriptive analysis concluded that **Pb, Zn** and **Cd** were to be categorized into a separate group of elements that indicated influence of anthropogenic activities while **As** was in a different group indicating natural origin. The geochemical maps depicting spatial variability in integrated potential ecological risk (PER) of heavy metals in Hyderabad, Pakistan, as developed in this study, can serve as valuable tools for government officials, policymakers, and stakeholders in guiding future planning and research and development (R&D) activities.

6. RESEARCH GAPS

Some research gaps observed are:

1. Lack of longitudinal studies on heavy metal trends.
2. Unclear sources of contamination in specific urban areas.
3. Insufficient investigation into effective soil remediation strategies.
4. Limited understanding of the impact of rapid urbanization on metal concentrations.
5. Need for comprehensive assessment of health risks associated with heavy metal exposure in urban soils.

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