



# Spatial distributions, sources, and ecological risks of metals in soils from the largest industrial city of Ulsan, South Korea

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**Abstract** The levels, contamination degrees, and spatial distributions of 13 metals—aluminum (Al), arsenic (As), barium (Ba), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn)—were investigated in soils from suburban, urban, and industrial sites in Ulsan, the largest multi-industrial city in South Korea. At the industrial sites, the mean concentrations of As (13.4 mg/kg), Cd (1.49 mg/kg), Cu (129 mg/kg), Ni (12.8 mg/kg), Pb (122 mg/kg), and Zn (376 mg/kg) were higher than those at the urban and suburban sites. In particular, soils from the non-ferrous metal and petrochemical industrial complexes were highly contaminated with As, Cd, Cu, Pb, and Zn, as supported by spatial distributions and multiple pollution indices. Ecological risks, assessed using the potential ecological risk index (RI), were very high at six industrial sites (913–1748), while those at the suburban (214–476) and

urban sites (187–518) were at moderate to considerable levels. On average, Cd and As contributed 70% and 17% of the total ecological risks, respectively. According to the principal component analysis, As, Cd, Cu, Pb, and Zn were significantly associated with industrial soils, suggesting that industrial emissions are the primary source, whereas Al, Co, Cr, Fe, Mn, Ni, and V were not significantly affected by industrial activities or vehicular emissions. The results highlight the need for remediation strategies in the industrial complexes to mitigate severe ecological risks in soils and prevent further contamination of other environmental media and ecosystems.

**Keywords** Metals · Soil contamination · Pollution index · Source identification · Industry

## Introduction

Metal contents in urban soils have increased sharply due to several factors, including industrial activities, municipal waste, fossil fuel combustion, and vehicle emissions, alongside rapid urbanization and industrialization worldwide (Binner et al., 2023; Zheng et al., 2023). Despite the high buffering capacity of soil and groundwater, elevated metal levels in soils have posed direct and indirect negative effects on public health and ecosystems, because they can be readily transferred to living organisms via suspended dust or direct contact (Tchounwou et al., 2012). Some metals,

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including copper (Cu), manganese (Mn), and zinc (Zn), are vital micronutrients for plant metabolism, but long-term and high accumulation in soils can still cause severe soil corrosion, phytotoxicity, and bioaccumulation in living organisms (Sharma et al., 2007; Wieczorek et al., 2023). Arsenic (As), cadmium (Cd), chromium (Cr), Cu, nickel (Ni), lead (Pb), and Zn are among the most anthropogenically enriched metals in soils at contaminated sites (Cho et al., 2019; Wieczorek et al., 2023). Surface water and groundwater are also at risk of contamination (Nduka et al., 2023; Park & Choi, 2021). These metals can negatively affect crop production through biomagnification and bioaccumulation in the food web.

Urban activities in metropolitan areas have resulted in soils characterized by disturbed profiles and altered physical properties, as well as metal contamination from diverse sources (Siegel, 2002). Therefore, the levels, spatial distributions, and pollution sources of metals in urban and industrial soils have been widely investigated (Binner et al., 2023). For example, in Guangdong, China, concentrations of As, Cd, Cu, Pb, and Zn in urban topsoils exceeded background levels by two to sixfold, with Cd and As particularly elevated above soil risk screening values due to mining, smelting, and traffic sources (Liang et al., 2023). Elevated levels of As and Pb in urban surface soils from Medak, India, were linked to industrial activities, vehicle emissions, and urbanization processes (Adimalla, 2020). Concentrations of As, Cd, Cu, Pb, Ni, and Zn in urban surface soils of Connecticut, USA, exceeded limits for direct human exposure due to industrial activities, historical pollution, and urban development (Butler et al., 2023). Similarly, soils from historical and recent industrial and mining regions in Salgótarján and Ózd, Hungary, were elevated for Cd and Pb (Abbaszade et al., 2023). These studies across diverse geographical regions highlight the importance of continued research on soil pollution assessment and monitoring strategies in metropolitan environments.

According to the Korean soil contamination survey and the soil monitoring network, metal levels in industrialized regions such as Ulsan were several-fold higher than those in farming areas (MOE, 2012). Ulsan, one of the metropolitan cities in Korea, has hosted four large industrial complexes (petrochemical, automobile, non-ferrous, and shipbuilding/heavy industries) since 1962. These industrial complexes have been in continuous

operation for five to six decades with no major structural changes. Due to long-term industrial operations and a high population density of 1.1 million, industry-derived organic contaminants in soils have been a major environmental concern in Ulsan (Cho et al., 2024; Kim et al., 2019; Kwon & Choi, 2014; Nguyen et al., 2016). Residential districts are located close to the industrial complexes, particularly along the southeast part of the city. Non-ferrous metal refineries are major sources of metal contamination in Ulsan Bay sediments, which have shown high ecological risk dominated by Cd (Chae et al., 2014; Ra et al., 2014). In addition, atmospheric Cd and Pb concentrations in the petrochemical and non-ferrous industrial complexes in Ulsan from 2006 to 2015 were higher than those in urban areas (Sung et al., 2018). Moreover, blood Pb and urine Cd levels were much higher among residents living near the industrial complexes than among non-exposed residents (Kim et al., 2017). These previous studies suggest that heavy metal contamination in Ulsan reflects both legacy pollution accumulated over decades and ongoing contributions from industrial activities. However, even though soil is well known to play an important role as a sink for inorganic and organic pollutants from the atmosphere, few studies on soils have been conducted in Ulsan. Therefore, soil monitoring and ecological risk assessment of metals in Ulsan are critical to reduce pollutant input into ground and river water and to prevent entry into food chains.

This study aimed to determine the levels, contamination degrees, and spatial distributions of metals in soils from the major industrial city of Ulsan. Industrial soils were collected at 10 sites in the major industrial complexes, and data from industrial regions were compared with those from 5 suburban sites to 10 urban sites with high population density and traffic volumes. Various pollution indices and statistical analyses were applied to (1) evaluate metal contamination and ecological risks in soils in this area, (2) investigate spatial patterns, and (3) identify potential sources.

## Materials and methods

### Soil sampling

Topsoil samples (0–10 cm depth) were collected from 25 sampling sites in Ulsan, South Korea, in July

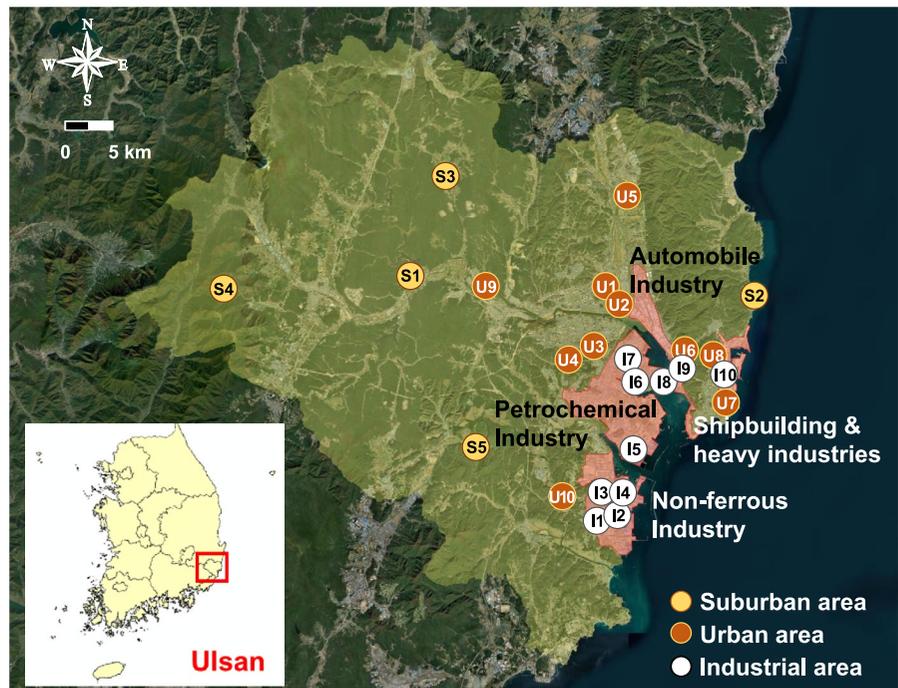
2012, including 5 suburban, 10 urban, and 10 industrial sites (Fig. 1). Industrial soil samples were taken from the non-ferrous (I1–I4), petrochemical (I5–I8), automobile (I9), and shipbuilding/heavy (I10) industrial complexes. Ten urban soil samples (U1–U10) were collected from highly populated administrative districts. Suburban soil samples (S1–S5) were collected from areas with low population density, located 4–25 km from the nearest industrial complex. Detailed site descriptions, coordinates, and soil types are provided in Table S1 in the Supplementary Information. The soil samples were classified into three soil types (Cambisols, Gleysols, and Luvisols) based on the Korean Soil Information System (<https://soil.rda.go.kr/eng/atlas/classification.do>), following the World Reference Base for Soil Resources. At each site, approximately 100 g of soil was collected from five points arranged in a cross pattern, with one point at the center and four points located 5 m away in the cardinal directions. Before sampling, organic debris was removed from the soil surface. The plastic shovels used for sampling were cleaned between sites to prevent cross-contamination. The collected samples were homogenized, air-dried, sieved through a 2 mm mesh, stored at  $-20\text{ }^{\circ}\text{C}$ , and analyzed within one month.

Pretreatment and instrumental analysis

For metal analysis, a 2 g soil sample was digested with 9 mL HCl and 3 mL  $\text{HNO}_3$  in Teflon vessels using a graphite digestion system (Odlab 98-002P, Korea) at  $200\text{ }^{\circ}\text{C}$  for 2 h (Cho et al., 2019). The digests were analyzed in triplicate using an inductively coupled plasma-optical emission spectrometer (ICP-OES; Varian 720 ES, USA). RF power, nebulizer gas flow, and auxiliary gas flow rates were set to 1200 W, 0.7 L/min, and 1.5 L/min, respectively. Target metals include aluminum (Al), As, barium (Ba), Cd, cobalt (Co), Cr, Cu, iron (Fe), Mn, Ni, Pb, vanadium (V), and Zn.

Instrumental detection limits (IDLs) and method detection limits (MDLs) were determined following the procedure suggested by the US EPA (1994). All sample concentrations exceeded the respective MDLs. Calibration curves for each metal showed coefficients of determination ( $R^2$ )  $> 0.999$  over the range of 0.05–10 mg/L. For method validation, the target metals in the standard reference material (SRM 2711a, NIST, USA) were analyzed using the optimized method. Recovery rates for each acid-extractable metal were higher than those reported in the US EPA Contract Laboratory Program study, which used

**Fig. 1** Locations of soil sampling sites for metal monitoring in Ulsan, South Korea: 5 suburban (S1–S5), 10 urban (U1–U10), and 10 industrial (I1–I10) sites. The basemap was generated using ArcGIS 10.4.1 (Esri, USA) orthophotography



diluted acids (50% HNO<sub>3</sub> and 20% HCl) for digestion at 95 °C for 30 min under gentle reflux in an open system, using the same SRM (Mackey et al., 2010). The accuracy and precision are presented in Table S2.

### Metal pollution assessment

Metal contamination was evaluated using the geoaccumulation index ( $I_{geo}$ ), defined as:

$$I_{geo} = \log_2 \left( \frac{C_{sample}^i}{1.5 \times C_{background}^i} \right) \quad (1)$$

where  $C_{sample}^i$  and  $C_{background}^i$  (mg/kg) are the measured and background concentrations of metal  $i$ , respectively (Canpolat et al., 2022). Background concentrations and classification criteria for  $I_{geo}$  are listed in Tables S3 and S4, respectively. Background metal concentrations were defined using the first quartile (25th percentile) values from the national soil monitoring program (MOE, 2012). For metals not included in the national monitoring, crustal abundance values (Taylor, 1964) were applied. This background reference was selected because of its temporal proximity to the designation of Ulsan as a specific industrial zone in 1962, enabling the assessment of long-term contamination.

To assess anthropogenic influence on topsoil metal content, the enrichment factor (EF) was calculated as follows:

$$EF = \frac{(C_i/C_{Fe})_{sample}}{(C_i/C_{Fe})_{background}} \quad (2)$$

where  $(C_i/C_{Fe})_{sample}$  and  $(C_i/C_{Fe})_{background}$  represent the concentration ratios of metal  $i$  to Fe in the soil sample and Earth's crust, respectively (Deliboran et al., 2024). Fe was selected as the reference element due to its crustal dominance and lower susceptibility to anthropogenic contamination in the study area, whereas Al may be influenced by aluminum alloys from the automotive and shipbuilding industries in Ulsan, South Korea. EFs between 0 and 2 suggest a crustal or natural origin, whereas values above 2 indicate likely anthropogenic sources. Specifically, EFs of  $2 \leq EF < 5$ ,  $5 \leq EF < 20$ ,  $20 \leq EF < 40$ , and  $EF \geq 40$  indicate moderate, significant, very high, and extremely high enrichment, respectively (Table S5).

Soil metal pollution can be evaluated by comparing metal concentrations with background levels or by quantifying pollutant accumulation using indices. In this study, the pollution index (PI), which relates sample concentrations to relevant background values, was applied (Varol et al., 2025). The PIs were calculated as the ratio of metal concentration in the sample ( $C_{sample}^i$ ) to the background concentration ( $C_{background}^i$ ):

$$PI = C_{sample}^i / C_{background}^i \quad (3)$$

In addition, the Nemerow integrated pollution index (NIPI), a widely used metric for assessing soil metal contamination (Nemerow, 1985), was calculated as follows:

$$NIPI = \sqrt{\left( \frac{(PI_{avg})^2 + (PI_{max})^2}{2} \right)} \quad (4)$$

where  $PI_{avg}$  is the mean PI of all metals ( $PI_i$ ), and  $PI_{max}$  is the maximum PI among them. The evaluation criteria for PI and NIPI are listed in Table S6.

For assessing the potential ecological risk posed by metals in topsoil, the potential ecological risk index (RI) was employed (Hakanson, 1980). RI is the sum of metal-specific ecological risk factors ( $E_r^i$ ), calculated by:

$$RI = \sum_{i=1}^n E_r^i \quad (5)$$

$$E_r^i = T_r^i \times PI \quad (6)$$

where  $T_r^i$  is the toxic-response factor for each metal (As=10, Cd=30, Cu, Pb, and Ni=5, Cr=2, and Zn=1) (Hakanson, 1980). The classification criteria for RI and  $E_r^i$  are provided in Table S7.

Both  $E_r^i$  and RI are commonly used for quantitative evaluation of ecological risks posed by soil pollutants (Deliboran et al., 2024; Varol et al., 2021). These indices reflect not only the anthropogenic contributions to metal accumulation in topsoil following urbanization, but also the biological toxicity of different metals. Therefore, they provide comprehensive insights into metal contamination in urban and industrial soils.

Statistical analysis

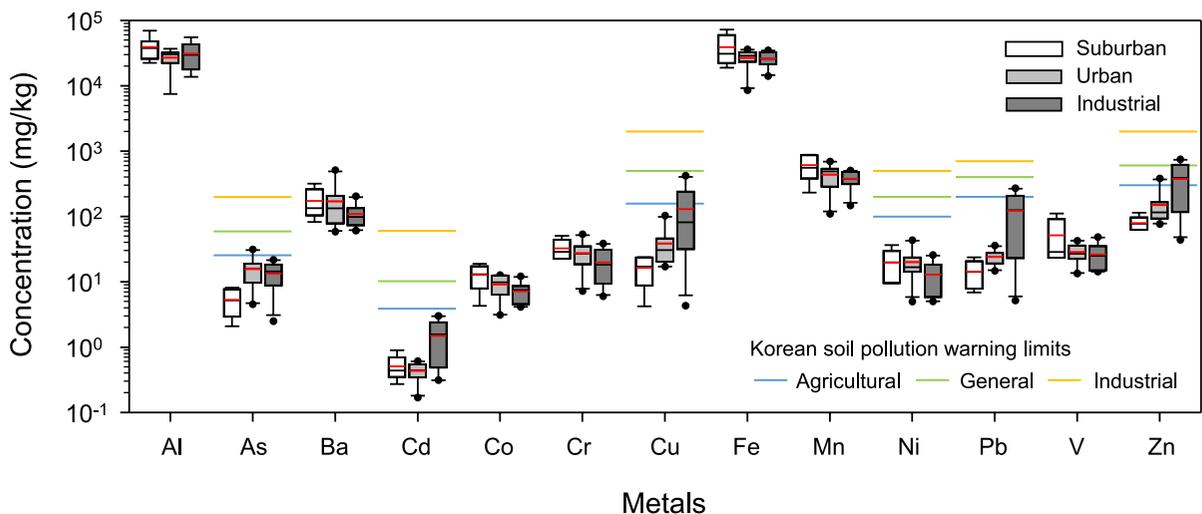
The normality of data distributions was assessed using Shapiro–Wilk tests. For normally distributed data, t-tests were employed to compare regional differences in mean metal concentrations, while Mann–Whitney rank-sum tests and ANOVA on ranks were used for non-normally distributed data. These statistical tests were performed using SigmaPlot 14.0 (Systat Software Inc., USA). Spearman correlation analysis and principal component analysis (PCA) were conducted using OriginPro 2020 (OriginLab, USA) and SPSS 25 (IBM, USA), respectively. PCA reduces the original dataset into a few explainable factors, capturing the variance and key information to help understand contamination patterns of each metal. The concentration profiles of 11 metals across 25 samples were used as input data for PCA. The first three components with eigenvalues greater than one were selected for data interpretation. To confirm the suitability of the correlation structure for PCA, the Kaiser–Meyer–Olkin (KMO) test was performed, and both the overall and individual KMO values exceeded 0.5. In addition, Bartlett’s test of sphericity was statistically significant ( $p < 0.01$ ).

Results and discussion

Levels and spatial distributions of metals

Site-specific concentrations of Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn are listed in Table S8, and their respective boxplots are presented in Fig. 2. The total ( $\Sigma_{13}$ ) metal concentrations were higher at the suburban sites (mean  $\pm$  standard deviation:  $77.9 \pm 39.6$  g/kg) than at the urban ( $55.4 \pm 16.8$  g/kg) and industrial sites ( $57.4 \pm 19.2$  g/kg). However, the differences among the sites were not statistically significant (ANOVA on Ranks,  $p > 0.05$ ) due to the high variability observed at the suburban sites. This pattern reflects elevated concentrations of rock-forming elements (e.g., Al, Ba, Fe, and Mn), which are abundant in crustal materials (Taylor, 1964). Among these elements, Al (31,111 mg/kg) and Fe (28,947 mg/kg) together accounted for 99% of the total metal mass. For trace metals (As, Cd, Co, Cr, Cu, Ni, Pb, V, and Zn),  $\Sigma_9$  metal concentrations at the industrial sites (mean: 708 mg/kg) were significantly higher than those at the urban (mean: 314 mg/kg) and suburban sites (mean: 232 mg/kg) (t-test,  $p < 0.05$ ), indicating predominant emissions from industries.

The Korean soil pollution warning limits for six metals (As, Cd, Cu, Ni, Pb, and Zn) are classified into three categories according to the Act on



**Fig. 2** Box plots of metal concentrations at the suburban (n=5), urban (n=10), and industrial (n=10) sites. The red line in each box represents the mean concentration. The yel-

low, green, and blue lines denote the Korean soil pollution warning limits for agricultural, general, and industrial soils, respectively

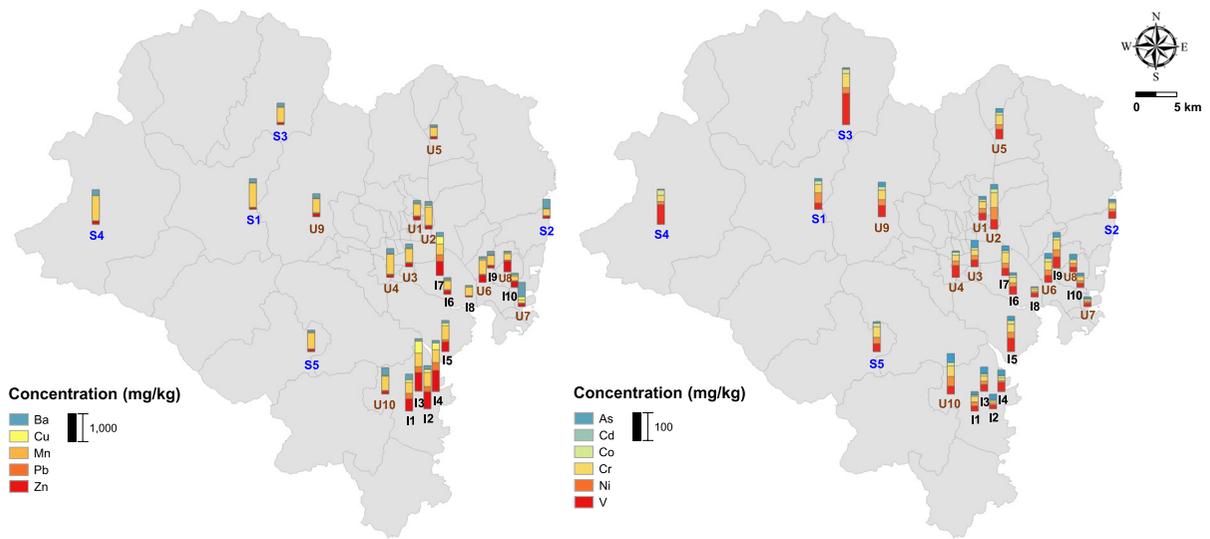
the Construction and Management of Geospatial Data: agricultural soil, general soil, and industrial soil (Fig. 2). At the industrial sites, the median concentrations of As (14.4 mg/kg), Cd (1.5 mg/kg), Cu (81.6 mg/kg), Ni (12.8 mg/kg), and Pb (125 mg/kg) were below the Korean limits for agricultural soil (25, 4, 150, 100, and 200 mg/kg, respectively). In contrast, the median Zn concentration (387 mg/kg) exceeded the standard for agricultural soil (300 mg/kg). At the suburban (5.2, 0.5, 17.0, 19.8, 14.1, and 77.2 mg/kg) and urban sites (15.9, 0.4, 30.5, 16.6, 24.1, and 115 mg/kg for As, Cd, Cu, Ni, Pb, and Zn, respectively), the concentrations were lower than the corresponding standards. When the concentrations at the suburban, urban, and industrial sites were compared with the corresponding pollution standards, none of these sites exceeded the thresholds.

Compared across land use types, the mean concentrations of As, Cd, Cu, Pb, and Zn at the industrial sites (13.4, 1.5, 129, 122, and 376 mg/kg, respectively) were significantly higher than those at the suburban sites (5.3, 0.5, 16.3, 14.3, and 79.4 mg/kg) (t-test and Mann–Whitney rank-sum test,  $p < 0.05$ ). The urban sites (mean: 15.7, 38.4, 24.2, and 150 mg/kg for As, Cu, Pb, and Zn) also showed higher concentrations than the suburban sites (t-test and Mann–Whitney rank-sum test,  $p < 0.05$ ). Since most urban sites are located within 3 km of the industrial areas (except U5 at 5 km and U9 at 10 km), they are likely influenced by heavy traffic and industrial emissions. In contrast, the suburban sites, located on average 15 km from the industrial complexes, were less affected. Ni concentrations did not differ significantly among the three site groups, suggesting minimal anthropogenic influence.

The mean concentrations of metals in this study were compared with those from other cities in several countries (Table S9). Overall metal concentrations at the urban and suburban sites in this study were comparable to or lower than those reported in Korea and other countries (Adhikari et al., 2024; Goncharov et al., 2024; Plak et al., 2024; Yao et al., 2024). However, the mean As concentration at the urban sites in Ulsan (15.7 mg/kg) was 2–3 times higher than values reported in Kraków, Lublin, and Toruń, Poland (5.6 mg/kg) (Plak et al., 2024), Chongqing, China (6.49 mg/kg) (Yao et al., 2024), and Bashkortostan, Russia (6.49 mg/kg)

(Goncharov et al., 2024), indicating relatively high As pollution in Ulsan. The industrial sites in Ulsan also showed elevated concentrations of As, Cd, Cu, Pb, and Zn, being 2.3, 3.8, 4.2, 3.5, and 3.2 times higher than the mean concentrations in the previous studies. The concentrations of Cd, Cu, Pb, and Zn at the non-ferrous industrial sites in Ulsan (mean: 2.5, 210, 212, and 610 mg/kg, respectively) were comparable to those reported for soils near an ore smelter (mean: 2.5, 111, 199, and 1,018 mg/kg, respectively) (Long et al., 2021). This result suggests that Cd–Cu–Pb–Zn co-enrichment is a characteristic signature of non-ferrous smelting activities across different regions. Although some heavily contaminated sites exhibited extremely high concentrations of As, Cd, Cr, Cu, Ni, Pb, and Zn (58.3, 46.6, 1,750, 50,900, 37,000, 44,500, and 48,700 mg/kg, respectively) (Adhikari et al., 2024; Plak et al., 2024), the levels at the industrial sites in Ulsan were generally high. Overall, the industrial areas in Ulsan were relatively contaminated with As, Cd, Cu, Pb, and Zn, whereas Cr and Ni remained at background levels, indicating negligible contributions of industrial emissions of these metals to soil.

Except for Al and Fe, spatial distributions of 11 metals are shown in Fig. 3 and each metal in Fig. S1 in the Supplementary Information. Al and Fe were excluded from Fig. 3 because their much higher concentrations hindered clear visualization of other metals. The  $\Sigma_{11}$  metal concentrations in the non-ferrous and petrochemical industrial areas (mean: 1,336 mg/kg) were higher than those in other areas (mean: 915 mg/kg). The high standard deviation (562 mg/kg) at the industrial sites suggests varying impacts among industrial complexes. Among individual metals, As, Cd, Cu, Pb, and Zn were strongly affected by industrial emissions. Notably, the concentrations of Cu, Pb, and Zn were elevated in the non-ferrous industrial area, consistent with atmospheric emission patterns (Fig. S1). Elevated levels in other industrial complexes also suggest that historical emissions may have exceeded current levels. In contrast, Ni and V concentrations were relatively low, even in petrochemical facilities. Although Ni and V are commonly used as refinery indicators, their low concentrations in Ulsan soils suggest either historically low emissions or limited deposition.



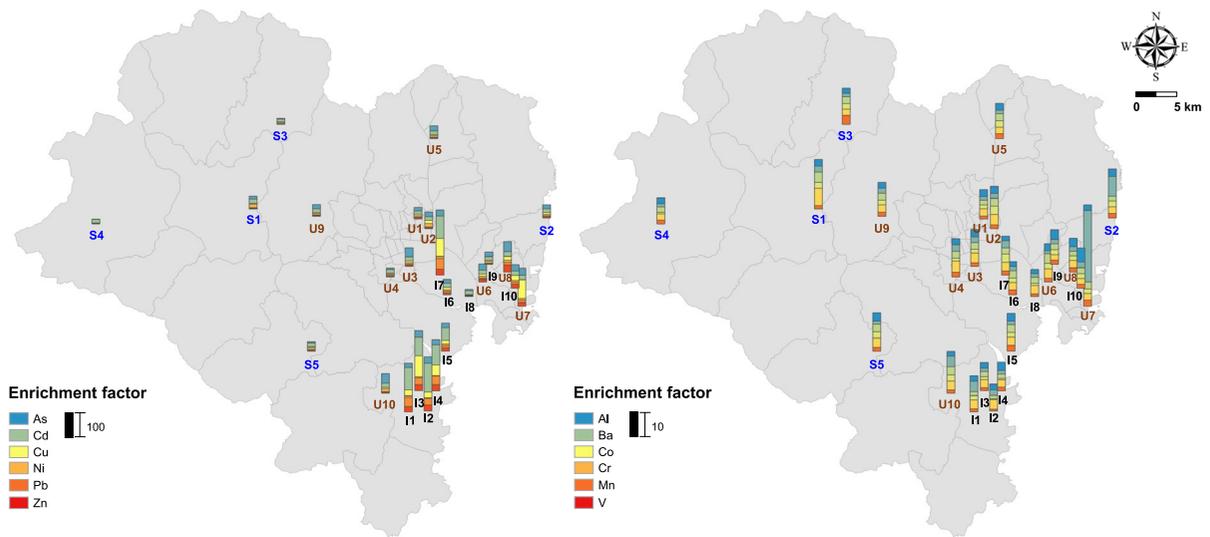
**Fig. 3** Spatial distribution of 11 metals (As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn) in soils across the study area

### Metal pollution assessment

The  $I_{geo}$  values suggest that soil contamination in Ulsan ranged from uncontaminated to extremely contaminated for the target metals (Table S10). The suburban, urban, and industrial sites were unpolluted by Al, Ba, Co, Cr, Fe, Mn, and V. For Cd, the suburban (mean: 2.4), urban (mean: 2.2), and industrial (mean: 3.6) sites were moderately to heavily polluted. The industrial sites were moderately to heavily contaminated by As (mean: 2.3), Cu (mean: 2.2), Pb (mean: 1.7), and Zn (mean: 1.7), whereas the urban and suburban sites were generally unpolluted by these metals, except for As in the urban areas (mean: 2.5).

The levels and spatial distributions of EF are presented in Table S11 and Fig. 4. The EFs for Al, Ba, Co, Cr, Mn, and V at the suburban, urban, and industrial sites ranged from 0 to 2, suggesting that these metals primarily originate from crustal materials or natural processes such as rock weathering, soil erosion, and biogenic processes. On the other hand, the EFs for As, Cd, Cu, Ni, Pb, and Zn at all sites indicated enrichment from various anthropogenic activities. The total EF of 12 metals was 2.1 times higher in the non-ferrous industrial complex (mean: 197) than in other industrial complexes (mean: 94.3), with the highest total EF observed at 17 (225) in the petrochemical industrial complex. Among individual metals, Cd exhibited the highest

mean EF (29.2), followed by As (17.1), Cu (16.3), Pb (9.29), Zn (9.01), and Ni (5.85). In particular, the suburban (12.8), urban (15.6), and industrial (51.0) sites showed the highest mean EFs for Cd, indicating extreme enrichment at the industrial sites. The EFs for Cd at the industrial sites were significantly higher than those at the suburban (t-test,  $p < 0.05$ ) and urban sites (Mann–Whitney rank-sum test,  $p < 0.05$ ), reflecting substantial deposition from anthropogenic sources. Elevated EFs of Cd (mean: 19.9) in soils of three industrial cities (Ulsan, Pohang, and Gwangyang) in Korea were also reported (Cho et al., 2019). According to the Korean soil contamination survey and the soil monitoring network, the Cd concentration in Ulsan (mean: 1.80 mg/kg) was 2.1 times higher than the national levels (mean: 0.84 mg/kg) (MOE, 2012), supporting industrial contamination as a primary source of Cd in Ulsan. Cd likely accumulated in soil through non-point sources such as roadside dust from tires and brake pads, industrial wastewater, and leaching from waste stockpiles and landfills (Kim et al., 2020). For As and Cu, the urban (mean: 22.0 and 12.7, respectively) and industrial (mean: 17.4 and 26.5) sites exhibited significant to very high enrichment. The industrial soils showed high EFs for Pb and Zn (mean: 17.9 and 14.1), whereas the suburban (mean: 2.01 and 2.41) and urban soils (mean: 4.29 and 7.22) had relatively low enrichment. These patterns indicate that industrial emissions in Ulsan



**Fig. 4** Spatial distribution of enrichment factors (EFs) of 12 metals

substantially contribute to soil contamination, with Cd showing the most widespread dispersal.

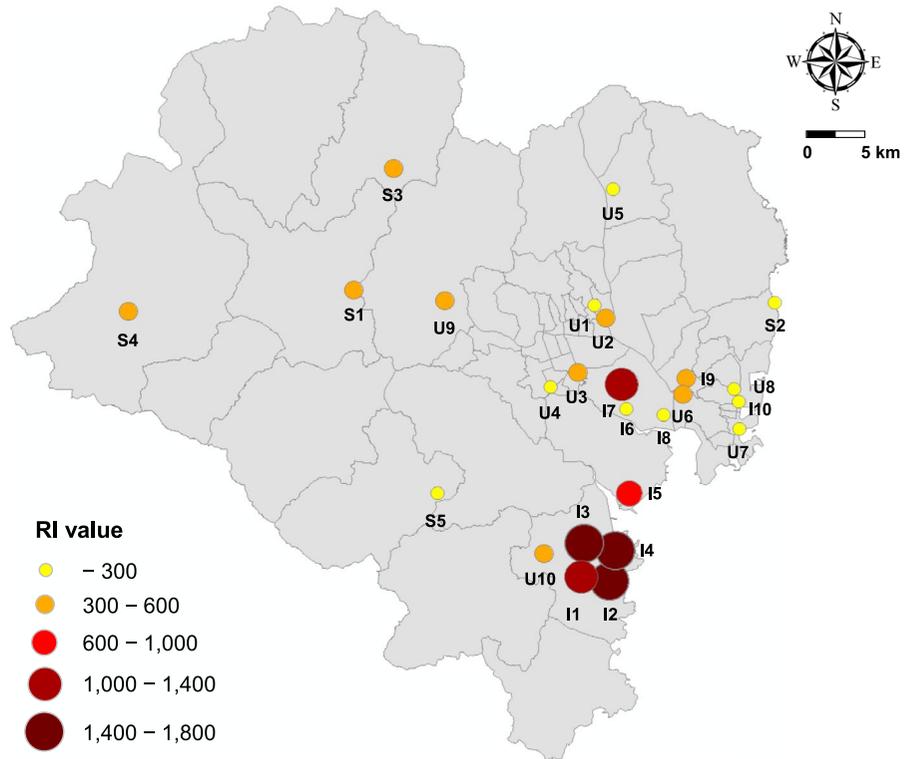
PIs varied considerably among metals (Table S12 and Fig. S2a). Across the industrial, urban, and suburban areas, 53% of soils were highly contaminated with As and Cd. The PI fractions were similar across all land-use types, with the mean contributions of major metals following the order Cd (32%) > As (21%) > Cu (13%) > Ni (9.1%) > Zn (8.7%) > Pb (7.5%). These results indicate that soils in all land-use types in Ulsan were mainly contaminated with As, Cd, Cu, Ni, Pb, and Zn. In previous studies, the PI fractions were Cd (33%), Cr (22%), Cu (16%), Zn (15%), and Pb (14%) (Gao et al., 2023), and Cd (35%), Pb (14%), Zn (14%), Ni (13%), Cr (12%), and Cu (11%) (Li et al., 2022). Compared with these studies, the PI fractions in Ulsan were characterized by a higher contribution of As and a lower contribution of Cr and Ni, consistent with the concentration comparisons. The NIPIs ranged from 3.69 to 10.7 (mean: 6.16) in the suburban soils, from 5.33 to 13.8 (mean: 7.98) in the urban soils, and from 4.11 to 35.9 (mean: 18.3) in the industrial soils (Fig. S2b). Previous studies reported mean NIPIs of 4.9 (Gao et al., 2023), 4.0 (Li et al., 2022), and 6.0 (Su et al., 2022), which were comparable to or slightly lower than those in the urban and suburban soils of Ulsan, but considerably lower than those in the industrial soils of Ulsan. The NIPIs among the three land-use types in this study

were not statistically different (ANOVA on Ranks,  $p > 0.05$ ), indicating that all sites were highly contaminated according to the index grades in Table S6. In summary, total EFs, total PIs, and NIPIs across all sampling sites were significantly correlated (Spearman correlation,  $p < 0.01$ ), as these multiple pollution indices exhibited similar spatial distribution patterns and comparable contamination levels throughout the study area.

#### Ecological risk assessment

The  $E_r^i$  values of each metal, RIs, and assessment grades are listed in Table S13, and the spatial distribution of RI is presented in Fig. 5. The mean  $E_r^i$  values from all soil samples decreased in the order: Cd (436) > As (78.3) > Cu (35.1) > Pb (21.7) > Ni (14.2) > Zn (4.02) > Cr (0.51). These results indicate that Cd posed high ecological risks in the suburban, urban, and industrial areas, while As in the urban and industrial soils could cause considerable risks. The  $E_r^i$  values of Cu and Pb in the industrial complexes also reached considerable risk levels, whereas those of the other metals were generally low across all land uses. The mean Cd risk levels were comparable to those reported in previous studies for urban and industrial areas, where risks were considered considerable to high, while the risks of the other metals (As, Cr, Cu, Ni, Pb, and Zn) remained low (Gao et al., 2023; Plak

**Fig. 5** Spatial distribution of the comprehensive potential ecological risk index (RI) of seven metals (As, Cd, Cr, Cu, Ni, Pb, and Zn). The RI was calculated as the sum of individual metal-specific ecological risk factors ( $E_i^i$ )



et al., 2024). In agreement with several pollution indices, Cd contamination was consistently identified in both previous studies and this study. Given that Cd has the highest toxicity factor of 30 (Hakanson, 1980) and its contamination is widespread across all land uses, continuous Cd monitoring is necessary even though its absolute concentrations are much lower than those of other metals.

The RI levels at the suburban (mean: 317, median: 303) and urban (mean: 361, median: 358) sites ranged from moderate to considerable, while those at the industrial sites (mean: 955, median: 1032) ranged from moderate to very high. Specifically, two industrial sites were classified as moderate, two as considerable, and six as very high ecological risks. Despite these differences, the RIs among the land-use categories were not statistically significant (ANOVA on Ranks,  $p > 0.05$ ), mainly due to high variability within each category. The RIs in this study were higher than those of four metals (Cd, Cu, Pb, and Zn) at urban sites in Istanbul, Türkiye (range: 82.5–265, mean: 135) (Sezgin et al., 2019) and those of seven metals in industrial, urban, and suburban areas in Poland (mean: 178) (Plak et al., 2024). The RIs of

seven metals in urban and industrial areas of Guangdong, China (range: 41.1–661, mean: 355) (Su et al., 2022) were comparable to those in this study. In both previous studies and the present study, the  $E_i^i$  values of Cd were consistently higher than those of the other metals.

In this study, the highest ecological risks were found at sites I1 (1,205), I2 (1,748), I3 (1,576), and I4 (1,723) in the non-ferrous industrial complex, as well as sites I5 (913) and I7 (1,152) in the petroleum industrial complex. These sites had a mean RI (1,386) much higher than those at the other sites (mean: 338), primarily due to Cd, which showed a 4.8-fold difference in concentrations. Cd concentration was strongly correlated with RI (Spearman correlation,  $r = 0.92, p < 0.01$ ). To examine the dispersion of contamination, linear regression analyses were conducted between the distance from the six most contaminated sites (I1, I2, I3, I4, I5, and I7) and the concentrations of the seven metals used for RI calculation (Fig. S3a), as well as the corresponding RIs (Fig. S3b). The metal concentrations exhibited a slightly decreasing pattern with distance but demonstrated no linearity ( $R^2 = 0.10$ ). Similarly, the RIs showed no relationship

with distance ( $R^2=0.06$ ), suggesting limited spatial dispersion of contamination from the identified pollution sources. This result indicates that atmospheric deposition from industrial and vehicular emissions weakly contributed to soil pollution in the urban and suburban areas. Heavy metals emitted from the industrial complexes in Ulsan are widely dispersed via atmospheric transport (Cho et al., 2025; Sung et al., 2018), potentially resulting in relatively uniform deposition patterns that attenuate spatial gradients in soil contamination. Instead, the contamination patterns suggest limited dispersion of metals, with contamination concentrated within the industrial complexes, potentially including accidental spills, improper waste disposal, and direct soil contamination during past operations (Yuan et al., 2019). Further investigation using sequential extraction techniques (Cipullo et al., 2018) is recommended to assess the bioavailability of metals for a more comprehensive evaluation of ecological risks.

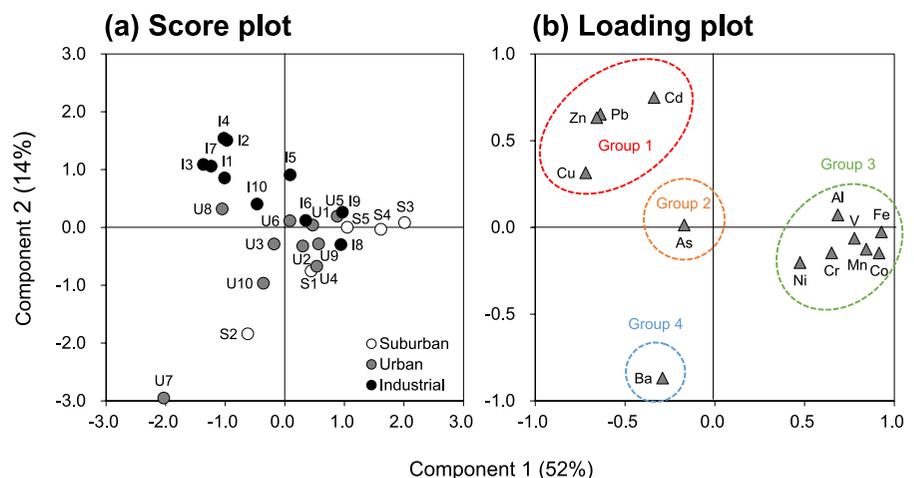
#### Source identification

The first two PCs, accounting for 52% and 14% of the total variance, respectively, were used to interpret the PCA results. The third PC (PC3), explaining 12% of the variance, increased the total explained variance from 66% (2D PCA) to 78% (3D PCA) (Fig. S4). However, the scattering patterns observed in the 2D PCA were largely consistent with those in the 3D analysis, indicating that the first two PCs were sufficient to interpret the patterns of metals in the study area. The score plot (Fig. 6a) showed that

the industrial soils were generally separated from the urban and suburban soils, while the urban and suburban soils, despite some overlap, were largely distinguishable from each other. A clear trend was observed where the industrial and suburban soils were mostly located in the upper-left and lower-right regions of the score plot, corresponding to negative PC1 and positive PC2 values and positive PC1 and negative PC2 values, respectively. The urban soils were generally concentrated near the center of the score plot. In addition, all industrial soils, except for I8, were positioned in the upper region of the score plot (with positive PC2 values) and were separated from most urban and suburban soils.

The scattering patterns of the soil samples can be explained by the distribution of metals in the loading plot (Fig. 6b). The target metals were categorized by PC1 into four groups: Group 1 (Cd, Cu, Zn, and Pb), Group 2 (As), Group 3 (Al, Co, Cr, Fe, Mn, Ni, and V), and Group 4 (Ba). The score and loading plots indicated that sites I1, I2, I3, and I4 in the non-ferrous industrial complex and I7 in the petrochemical industrial complex were strongly associated with Group 1 metals. Notably, Korea Zinc in Ulsan, one of the world's largest non-ferrous metal producers, annually produces 26,400, 412,000, and 640,000 tonnes of Cu, Pb, and Zn, respectively (<https://www.koreazinc.co.kr/en>). These metals are also released from diverse industrial activities, including Zn refining, smelting, steel alloys, oil paints, batteries, and electric contact devices (Chae et al., 2014; Qing et al., 2015). Additionally, LS MnM, hosting the largest copper smelter in Korea, is located in Ulsan with an annual

**Fig. 6** PCA results of metals in the soil samples from the three areas: **a** score plot and **b** loading plot



production capacity of 680,000 tonnes (<https://www.lsmnm.com/en/main>). The influence of these large-scale non-ferrous metal smelters on air and soil metal levels in Ulsan has been previously reported (Cho et al., 2019, 2023, 2025). For Group 2, As was positioned near the center of the loading plot, suggesting contamination from both industrial activities and urban sources such as vehicular emissions and residential activities (Rodland et al., 2023). In contrast, the urban and suburban soils were more characterized by Group 3 metals than the industrial soils. In particular, sites S3 and S4, located farthest from the city center, exhibited higher contributions from Group 3 metals, which likely represent natural metals. Sites S2 and U7, clearly separated from other urban and suburban soils along PC2, were characterized by a high fraction of Group 4 (Ba). These sites, located along the east coast, suggest influence from shipbuilding activities, where Ba is used in welding and painting

(WHO, 2001). Elevated Ba concentrations from port and shipping emissions have been reported previously (Chagas et al., 2025; Silveira et al., 2022).

Spearman correlation coefficients between metal concentrations at the 25 sites are presented in Fig. 7. Significant correlations were observed for As-Cu ( $r=0.53$ ), As-Pb ( $r=0.50$ ), As-Zn ( $r=0.60$ ), Cd-Pb ( $r=0.51$ ), Cd-Zn ( $r=0.56$ ), Cu-Pb ( $r=0.79$ ), Cu-Zn ( $r=0.83$ ), and Pb-Zn ( $r=0.88$ ), suggesting common sources related to metal processing and industrial activities (Chae et al., 2014; Qing et al., 2015). The significant correlations ( $p < 0.05$ ) of As with Cu, Pb, and Zn indicate potential contamination from coal combustion, non-ferrous metal smelting, and vehicular emissions (Rodland et al., 2023). Spatial pollution patterns (Fig. S1) further confirm that these metals were significantly affected by industrial emissions, consistent with PCA results (Fig. 6). At the industrial sites, these metals were significantly correlated

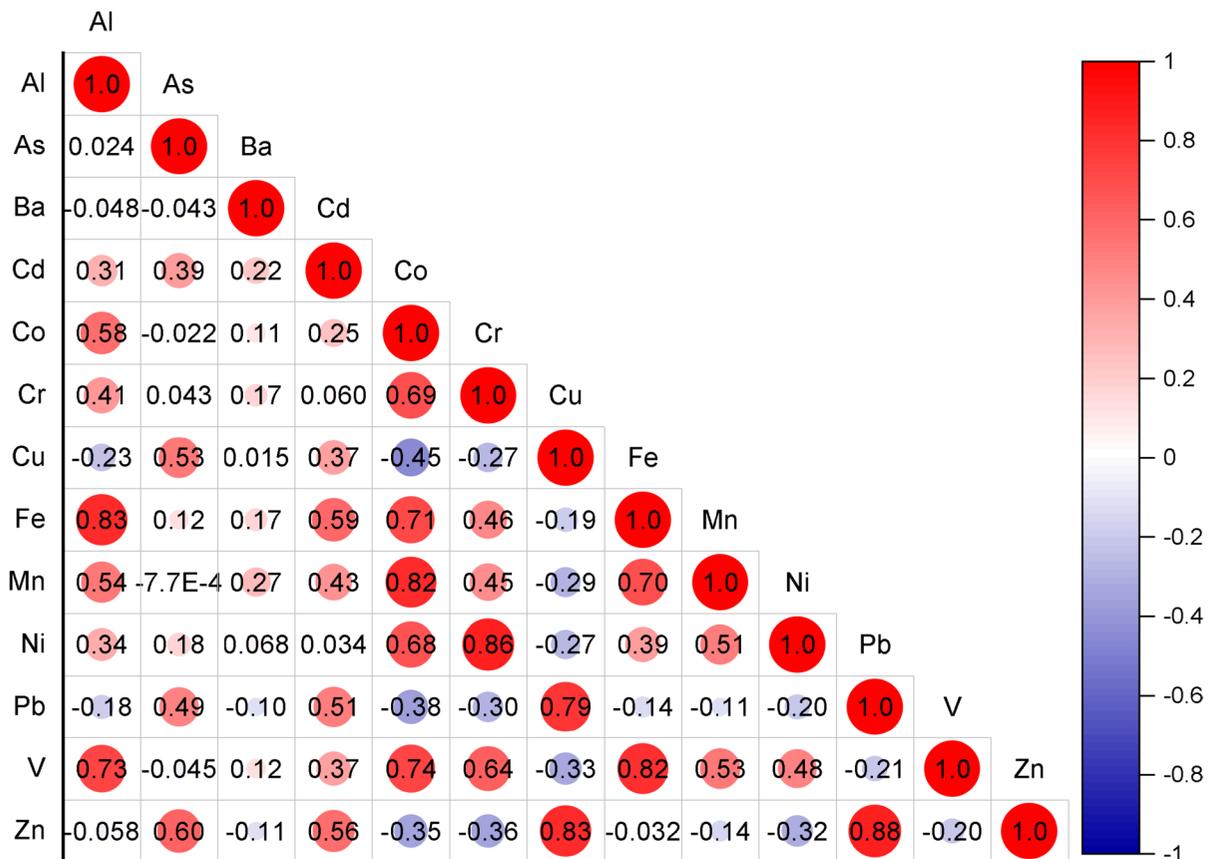


Fig. 7 Spearman correlation coefficients of metal concentrations in all soil samples

with each other ( $p < 0.05$ ) (Fig. S5a). Seven metals (Al, Co, Cr, Fe, Mn, Ni, and V) also showed significant correlations ( $p < 0.05$ ), consistent with the loading plot (Fig. 6b). Many of these are crustal or natural metals, and their total concentrations were not relatively high at the industrial sites (Fig. S1). PCA results indicated that these metals were more associated with the urban and suburban soils (Fig. 6), where concentrations of other metals remained lower. Correlations between Ba and other metals were not significant ( $p > 0.05$ ) within each land-use type, except for the Ba-Cr correlation observed in the suburban soils (Fig. S5), supporting the influence of distinct emission sources (e.g., shipbuilding), as discussed above.

Significant correlations ( $p < 0.05$ ) were also found for Cd-Fe ( $r = 0.59$ ), Cd-Mn ( $r = 0.43$ ), and Co-Cu ( $r = -0.45$ ). In this study, Cd and Cu are considered as industrial-emitted metals, whereas Co, Fe, and Mn are crustal or natural metals. Cd and Cu concentrations were higher at the industrial sites, while Co, Fe, and Mn concentrations remained relatively low (Fig. S1). Nevertheless, their spatial distribution patterns across Ulsan were still comparable. This similarity may be related to the role of Fe-Mn oxides, which act as primary carriers controlling Cd mobility through surface complexation and co-precipitation (Lu et al., 2022), thereby explaining the correlations between Cd and Fe/Mn rather than common anthropogenic sources. In contrast, Co-Cu correlations were not significant ( $p > 0.05$ ) when analyzed separately by area (Fig. S5). Overall, metal levels and profiles in Ulsan were strongly influenced by both industrial activities and heavy traffic.

The spatial patterns of metal contamination and source attribution in this study suggest that metal remediation strategies should be implemented, particularly in the non-ferrous and petrochemical industrial complexes with high ecological risks. The strong associations between industrial activities and certain metals (As, Cd, Cu, Pb, and Zn) indicate that source-specific management, particularly emission controls for Cd and As, the primary contributors to ecological risk, would be more effective. Although metal concentrations were below the Korean soil pollution warning limits, ecological risks were very high at several industrial sites. Regular monitoring programs should be established in high-risk areas, with particular attention to metal transfer to groundwater and river systems. Furthermore, the current soil quality

standards in South Korea, which serve as regulatory action levels, may need reevaluation to better account for cumulative ecological impacts of metals in the industrialized city of Ulsan, where residential areas are located close to the industrial complexes.

## Conclusion

Thirteen metals in the suburban, urban, and industrial soils in Ulsan, South Korea, were analyzed to investigate their spatial distributions, possible sources, and ecological risks. The metal concentrations were higher at the industrial sites than at the urban and suburban sites. The soil contamination was dominated by industrial emissions, with Cd identified as the primary contaminant from the industrial complexes. The contamination patterns indicated limited dispersion, reflecting direct industrial impacts. Considering that smelters in Ulsan are primarily distributed in the non-ferrous industrial complex, the smelting processes and waste disposal activities are likely major contributors of As, Cd, Cu, Pb, and Zn to the soils. The soils were heavily contaminated according to the applied pollution indices ( $I_{geo}$ , EF, PI, and NIPI). The ecological risks ( $E_r^i$  and RI) ranged from moderate to very high, with As and Cd posing significant threats to the ecosystems in and near the non-ferrous and petrochemical industrial areas. The non-ferrous industrial complex was identified as the main source of As, Cd, Cu, Pb, and Zn. The As originated from mixed anthropogenic sources, including both industrial activities and urban emissions. The other metals (Al, Co, Cr, Fe, Mn, Ni, and V) were attributed to natural weathering processes, while the Ba contamination was associated with the coastal shipbuilding activities. Since the soil contaminants can leach into the water systems or food chains, the findings of this study provide useful information for establishing risk-based assessment criteria for soil pollution, developing appropriate remediation strategies, and implementing continuous monitoring of the metals. Sequential extraction techniques and long-term monitoring programs are recommended to assess metal bioavailability and track contamination trends.

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**Data availability** No datasets were generated or analysed during the current study.

## Declarations

**Competing interest** The authors declare no competing interests.

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