

Spatial distribution, sources, and ecological risk of potentially toxic elements in granite-derived surface soils and river sediments of an agricultural watershed, Eastern China*

Qiugui WANG¹, Enzong XIAO¹, Penggao FANG², Qiangqiang ZHONG³, Jinli CUI¹, Tangfu XIAO^{1, **}, Siyi HU^{4, **}

¹Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education; School of Environmental Science and Engineering, Guangzhou University, Guangzhou 510006, China

²Donghai Laboratory, Zhoushan 316000, China

³Third Institute of Oceanography, Ministry of Natural Resources, Xiamen 361005, China

⁴School of Marine Sciences, Hainan University, Haikou 570228, China

Received Nov. 12, 2025; accepted in principle Jan. 2, 2026; accepted for publication Mar. 12, 2026

© Chinese Society for Oceanology and Limnology, Science Press and Springer-Verlag GmbH Germany, part of Springer Nature 2026

Abstract Potentially toxic elements (PTEs) in agricultural soils and river sediments pose major ecological risks. However, their distribution, sources, and geochemical behavior in subtropical granite derived watersheds remain insufficiently constrained. In this study, 15 surface soil and 12 river sediment samples were collected from a granitic watershed in Zhejiang Province, China, to investigate the spatial distribution, provenance, and ecological risks of seven PTEs (arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn)). The results show that PTE concentrations vary widely, in the range of 1.4–38.4 mg/kg for As, 0.05–1.32 mg/kg for Cd, 4.0–94.0 mg/kg for Cr, 2.5–37.0 mg/kg for Cu, 2.0–27.5 mg/kg for Ni, 21.5–108 mg/kg for Pb, and 56–202 mg/kg for Zn. Cr, Cu, and Ni exhibit decreasing concentrations from upstream to downstream, reflecting dominant lithogenic control by granite weathering, whereas Cd, Pb, and Zn show enrichment in midstream and downstream areas due to anthropogenic inputs. On average, river sediment Cd concentrations are 2.5 times higher than those in soils. Risk assessment indicates that several PTEs exceed regional background values, but Cd exhibits the strongest enrichment, with enrichment factor (EF) values up to 12.1. Ecological risk assessment based on an adjusted potential ecological risk index (RI) indicates that the watershed is generally characterized by low to moderate ecological risk. However, Cd contributes disproportionately to total ecological risk, accounting for 42.2%–82.5% (mean 73.8%) of the RI values, and midstream sediments represent clear risk hotspots. Multivariate statistical analyses distinguish lithogenic PTEs (Cr, Cu, Ni, Ti) with low mobility and residual enrichment from anthropogenic PTEs (Cd, Pb, Zn) exhibiting strong particle-associated transport and cumulative downstream accumulation. These results demonstrate that soil-sediment transfer amplifies Cd-dominated ecological risks in granite-derived agricultural watersheds and highlight the need for targeted agricultural management strategies.

Keyword: potentially toxic element; ecological risk; soil-sediment transport; granite weathering; anthropogenic pollution

1 INTRODUCTION

Potentially toxic elements (PTEs), including arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn), have

* Supported by the National Natural Science Foundation of China (Nos. 42373069, 42307280), the Qinghai Provincial Key Research and Development and Transformation Program (No. 2024-QY207), the Guangdong Special Support Program (No. 2024TX08A218), and the Science and Technology Foundation of Guangzhou City (No. 2025A04J3358)

** Corresponding authors: tfxiao@gzhu.edu.cn; syhu@hainanu.edu.cn

attracted increasing global attention due to their persistence, nonbiodegradability, and toxicity to both ecosystems and human health (Li et al., 2023; Wang et al., 2024; Yan et al., 2025). Even at trace concentrations, PTEs can accumulate in soils, migrate into aquatic systems, and pose long-term ecological risks through complex biogeochemical processes (Gao et al., 2021; Bertrand et al., 2024; Yang et al., 2024; Ye et al., 2025). In particular, elements such as As, Cd, Pb, and Cr are widely recognized for their adverse health effects, including carcinogenicity, neurotoxicity, and damage to renal and cardiovascular systems, mainly via prolonged exposure through contaminated soils, sediments, and agricultural products (Sobhanardakani, 2017; Khalijian et al., 2022; Saleh et al., 2022; Selahvarzi and Sobhanardakani, 2022). Their occurrence is generally controlled by both natural and anthropogenic inputs. Natural sources are related primarily to lithology, parent rock weathering, and pedogenic processes that define the regional geochemical background conditions (Augustsson et al., 2023; Wu et al., 2024; Wang, 2025). In contrast, anthropogenic activities such as mining and smelting (Zhou et al., 2022; Wei et al., 2023; Nie et al., 2025), fossil fuel combustion (Liu et al., 2024), agriculture (Peng et al., 2019; Yang et al., 2022; Wang and Ma, 2004), and traffic activities (Wang and Lu, 2011; Chen et al., 2024) often increase PTE accumulation and alter their chemical form, mobility, and bioavailability (Li et al., 2022; Ou et al., 2025; Fang et al., 2026).

Soils function as the principal reservoirs of PTEs, thereby integrating inputs from both geogenic and anthropogenic sources (Terzano et al., 2021; Adnan et al., 2025; Cao et al., 2025). The geochemical speciation of PTEs largely affects their mobility and ecological risks (Rubinos et al., 2021; Sakan et al., 2023; Yan et al., 2025). Lithogenic PTEs are generally retained in stable residual fractions, whereas anthropogenic inputs are often associated with more labile forms, yielding increased environmental hazards (Heltai et al., 2018; Yang and Lin, 2020; Sakan et al., 2023; Yan et al., 2025). Geological background conditions also affect enrichment, for example, soils derived from black shales often contain naturally high levels of Cd, As, and Pb (Cui et al., 2023; Wu et al., 2024; Wang, 2025), whereas in regions with lower natural background values, intensive agriculture activity and atmospheric deposition significantly increase Cd, Pb, and Zn levels (Peng et al., 2022; Gong et al., 2024; Li et al., 2025). Moreover, soils may act as secondary sources

of contamination, releasing PTEs into rivers via erosion and runoff processes (Bordas and Bourg, 2001; Yan et al., 2025). In aquatic systems, adsorption-desorption, complexation, mineral associations, and hydrodynamic processes regulate the partitioning of PTEs between particulate and dissolved phases, ultimately shaping their downstream fate (Bordas and Bourg, 2001; Miranda et al., 2022; Bertrand et al., 2024). Thus, understanding PTE sources, speciation, and soil-to-sediment transfer is essential for ecological risk assessment and sustainable land management.

Previous studies on PTEs have focused on large river basins, estuaries, and lacustrine systems (Li et al., 2023; Wang et al., 2023b; Bertrand et al., 2024; Yan et al., 2025). However, the complex lithological heterogeneity, hydrological connectivity, and overlapping anthropogenic inputs in these large-scale systems often obscure the relative contributions of natural and anthropogenic sources. In addition, climatic conditions and topographic variability further modulate secondary PTE redistribution in soils, complicating the interpretation of accumulation patterns and migration pathways (Wei et al., 2023; Sreelesh et al., 2025). In contrast, small watersheds are typically characterized by more homogeneous lithology, simpler hydrological networks, and clearer land use structures, providing well defined spatial boundaries for tracing PTE sources, transport, and transformation processes (Efthimiou et al., 2020; Zhang et al., 2022). These systems therefore represent sensitive natural laboratories for investigating PTE distribution, speciation, and soil-sediment interactions under relatively controlled geological and hydrological settings.

Granite terrains are particularly important in the study of soil and sediment contamination due to their unique weathering processes, which influence the mobilization and distribution of PTEs (Hou et al., 2020). In regions where granite-derived soils dominate, PTEs such as Cd, Pb, and As can become enriched through both natural weathering and anthropogenic activities (Sheng et al., 2025). These terrains often exhibit relatively low natural background concentrations of PTEs, but agricultural practices, such as the use of fertilizers and pesticides, can significantly amplify their concentrations, leading to ecological and health risks (Xu et al., 2021; Sheng et al., 2025). Understanding how PTEs behave in granite-derived landscapes is essential for assessing their environmental impact in subtropical regions.

Despite extensive investigations in black shale

regions and mining-impacted areas, the geochemical behavior and ecological risks of PTEs in granite-derived agricultural watersheds remain poorly constrained, particularly in small catchments characterized by intensive soil erosion and strong soil-sediment coupling. These knowledge gaps are especially evident in southeastern China, including Zhejiang Province, where both granite geology and agricultural activities contribute to PTE accumulation (Yang et al., 2022; Zhou et al., 2022; Li et al., 2023; Wu et al., 2024; Sheng et al., 2025). To address this gap, the present study investigates a representative small agricultural watershed in Songyang County, Zhejiang Province, underlain by relatively uniform granite-derived soils. By adopting an integrated soil-sediment system approach and combining spatial analysis, ecological risk assessment, and multivariate statistical methods, this study aims to elucidate the sources, transport processes, and geochemical behaviors of PTEs during soil erosion and fluvial transport. Particular attention is given to identifying dominant

contributors to ecological risk and exploring the mechanisms controlling their redistribution. The results are expected to advance the understanding of PTE dynamics in granite terrains and provide scientific support for environmental risk management in agricultural watersheds.

2 MATERIAL AND METHOD

2.1 Study area

Songyang County, located in Lishui City, Zhejiang Province, is recognized as a traditional agricultural county in southeastern China. The area is dominated by low mountainous and hilly terrain features under a subtropical monsoon climate, with notable vertical differences in climatic conditions. The mean annual temperature and precipitation are 17.7 °C and 1 700 mm, respectively. The investigated watershed is located in the eastern part of Songyang County (119°36'E–119°38'E, 28°22'N–28°28'N; Fig.1). The bedrock geology of the watershed is dominated by

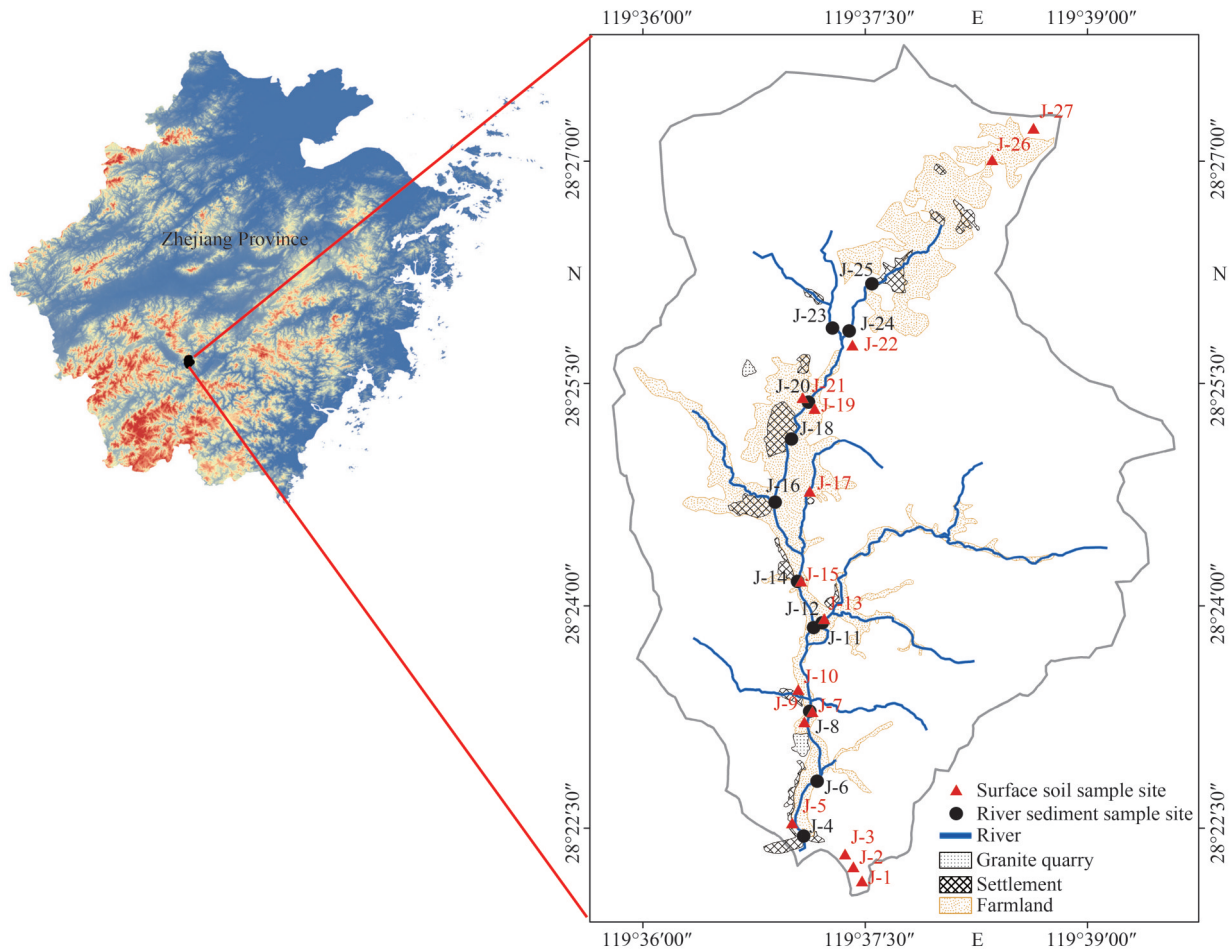


Fig.1 Location of the study area and sampling sites

Yanshanian granite intrusions, with minor occurrences of Jurassic rhyolite (Li et al., 2012). Settlements are sparsely distributed along riverbanks, where intensive agricultural activities including vegetable, rice, and tea cultivation are concentrated, resulting in notable anthropogenic disturbance superimposed onto a relatively uniform lithological background. The soils in the study area are classified as red soils, with pH values ranging from 4.11 to 6.59 and soil organic matter contents of 6.77–27.49 g/kg (Xu et al., 2021).

2.2 Sample collection and chemical analysis

Because the study area exhibits relatively stable geological and land-use conditions, sampling was conducted in September 2020 and October 2022. A total of 15 surface soil samples (0–20 cm) and 12 surface sediment samples (0–5 cm) were collected from the watershed (Fig.1). Soil samples were obtained using a stainless-steel coring ring (5-cm diameter×5-cm height) and stored in cloth bags. Surface sediment samples were obtained using a stainless-steel grab sampler and transferred into polyvinyl chloride tubes (5-cm height×10-cm diameter; Wang et al., 2023a). In the laboratory, soil samples were dried naturally at room temperature, whereas the sediment samples were freeze dried. All the samples were subsequently homogenized and sieved to particle sizes <100 mesh prior to analysis.

For digestion, ~125 mg of dried sample was placed in a closed Teflon vessel containing a mixed acid solution (HF (Guaranteed Reagent (GR), Guangzhou Chemical Reagent Factory, Guangzhou, China)+HCl (GR, Guangzhou Chemical Reagent Factory, Guangzhou, China)+HNO₃ (GR, Guangzhou Chemical Reagent Factory, Guangzhou, China)) and heated on a hotplate at ~180–200 °C until complete dissolution was achieved. The solution was evaporated to near dryness and reconstituted with 0.1-mol/L HNO₃ to a fixed volume (Wang et al., 2023b). Elemental concentrations were determined through inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7900, Agilent Technologies, USA). Quality assurance and quality control (QA/QC) were ensured via the use of procedural blanks, duplicates, and certified reference materials (GBM321-8, MRGeo08, OREAS-45h, and OREAS-25a, ALS company, Australia). The value of PTEs in certified reference materials were shown in Supplementary Table S1. The analytical precision, expressed as the relative standard deviation (RSD), was better than 10%, and the recoveries for the

reference materials ranged between 90% and 110%, thus confirming the reliability and accuracy of the analytical data.

2.3 Assessment of pollution and ecological risk

The enrichment factor (EF), geo-accumulation index (I_{geo}), Nemerow pollution index (NPI), and potential ecological risk index (RI) were employed to evaluate the contamination levels and associated ecological risks of PTEs in surface soils and river sediments. Given the small watershed scale and the strong coupling between soils and sediments, provincial soil background values were adopted as a conservative and consistent reference. Specifically, EFs were calculated using the background values of soils in Zhejiang Province (China Environmental Monitoring Center, 1990). The I_{geo} , NPI, and RI based on the risk screening values (RSVs) for agricultural soils (pH≤5.5) as defined in the Soil Environmental Quality Risk Control Standard for Agricultural Land, China (MEEC and SAMR, 2018). The rationale for applying soil-based reference values to sediments lies in the fact that sediments in small catchments are primarily derived from local soil erosion and hillslope processes. Thus, utilizing soil background values ensures a consistent and appropriate assessment of PTE enrichment and ecological risk across the entire watershed.

The EF was calculated to assess anthropogenic enrichment relative to natural background, as follows:

$$EF = \frac{(X/Ti)_{sample}}{(X/Ti)_{background}},$$

where $(X/Ti)_{sample}$ and $(X/Ti)_{background}$ are the element to titanium (Ti) ratios in the sample and background, respectively. Ti was chosen as the reference element because of its lithophilic nature, resistance to weathering, and minimal anthropogenic influence in granite weathering regions (Zozulya et al., 2022; Tepanosyan et al., 2024). EF values were categorized as in Supplementary Table S2 (Gope et al., 2018).

The I_{geo} index was calculated as follows (Müller, 1969):

$$I_{geo} = \log_2 \left(\frac{C_i}{1.5 \times C_0} \right),$$

where C_i is the measured concentration of element i and C_0 is its background value. The factor 1.5 is

introduced to minimize the effects of potential changes in natural background values due to lithological variations (Wang et al., 2023b). I_{geo} values are divided into seven classes as shown in Supplementary Table S2 (Müller, 1969).

The NPI allows the assessment of the overall degree of pollution of the soil and includes the contents of all PTEs, calculated as follows (Kowalska et al., 2018):

$$\text{NPI} = \sqrt{\frac{\left(\left[\frac{1}{n} \sum_{i=1}^n \frac{C_i}{C_0} \right] \right)^2 + \left(\left[\max \left(\frac{C_i}{C_0} \right) \right] \right)^2}{2}}.$$

NPI values are divided into five classes as shown in Supplementary Table S2 (Kowalska et al., 2018).

The RI proposed by Hakanson (1980) was used to assess ecological hazards (Hakanson, 1980), and this index can be expressed as:

$$\text{RI} = \sum_{x=1}^n E_r^x = \sum_{x=1}^n T_r^x \times C_f^x,$$

$$C_f^x = \frac{C_i}{C_0},$$

where E_r^x is the potential ecological risk factor for PTE x ; T_r^x is the toxic response factor for PTE x : Zn (1) < Cr (2) < Pb = Ni = Cu (5) < As (10) < Cd (30); and C_f^x is the contamination factor for PTE x . The ecological risk categories for E_r^x was summarized in Supplementary Table S2. The classification criteria for the potential ecological RI were referenced from Hakanson (1980). In this study, the RI classification thresholds were adjusted based on the specific set of seven PTEs investigated. Given that the sum of toxic response factors for these seven PTEs is 58 (compared to 133 in the original study), the adjusted RI thresholds were calculated by dividing the original Hakanson (1980) values by 2.29 (the ratio of 133 to 58). Details of the adjusted classification are provided in Supplementary Table S2.

3 RESULT

3.1 Descriptive statistics of trace elements and PTEs

The concentrations of Ti, As, Cd, Cr, Cu, Ni, Pb, and Zn in the surface soils and river sediments from the study area are summarized in Table 1. The mean concentrations of As, Cd, Cr, Cu, Ni, Pb, and Zn were 10.5 ± 8.5 , 0.413 ± 0.350 , 53.9 ± 22.6 , 17.1 ± 7.6 , 17.0 ± 6.9 , 44.9 ± 19.8 , and 131 ± 42 mg/kg, respectively. On average, higher concentrations of Cd, Cr, Cu, Ni,

and Zn were detected in the sediments than in surface soils. The coefficient of variation (CV) was applied to evaluate spatial variability across the sites. Notably, Ti exhibited the lowest variability with a mean of $0.553\% \pm 0.146\%$, and a CV of 26%, reflecting its lithogenic control and resistance to disturbance. Cr, Cu, Ni, Pb, and Zn exhibited moderate variability, suggesting intermediate spatial dispersion. As and Cd demonstrated high variability, indicating significant spatial dispersion across the sampling sites.

One-way ANOVA coupled with Levene's test and appropriate post-hoc analyses (independent samples t -test or Mann-Whitney U test) was applied to compare PTE concentrations between surface soils and river sediments (Supplementary Table S3). Levene's test confirmed homogeneity of variances for all elements ($F=1.07-3.52$, $P>0.05$). Significant differences were observed for Cd, Cr, and Ni. Sediment Cd concentrations were significantly higher than those in the surface soils (Mann-Whitney $U=30.0$, $P=0.002$), exceeding the surface soil levels by a factor of 2.52. Cr ($t=-2.36$, $P=0.024$) and Ni ($t=-2.12$, $P=0.039$) also showed significantly higher concentrations in the river sediments (by 42.9% and 37.5%, respectively). In contrast, no significant differences were detected for As, Cu, Pb, or Zn ($P>0.05$). These results indicate element specific migration and accumulation behaviors within the surface soil and river sediment system, with Cd showing pronounced enrichment in the river sediments and thus posing elevated ecological risk, whereas Cu and Zn exhibit relatively stable geochemical behavior across media.

To contextualize the measured concentrations, the results were compared with data from multiple reference datasets (Table 1). In surface soils, the mean concentrations of Ti, As, Cd, Pb, and Zn exceeded background soil concentrations in Zhejiang Province (China Environmental Monitoring Center, 1990). However, the concentrations of As, Cr, Cu, Ni, and Pb at all sampling sites were below the risk screening values for agricultural soils specified in the soil environmental quality risk control standard for soil contamination of agricultural land (MEEC and SAMR, 2018). In contrast, Cd exceeded the corresponding risk screening value at 44% of the sampling sites, indicating localized Cd contamination. In addition, Zn concentrations at sites J7 and J18 exceeded the agricultural soil risk screening threshold, suggesting potential site-specific enrichment.

Table 1 Statistical summary and background comparison of PTEs concentrations in surface soils and sediments from Zhejiang Province

	<i>N</i> ^a		Ti (%)	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Reference
Surface soils	15	Min	0.207	1.40	0.050	4.00	2.50	2.00	21.5	56.0	This study
		Max	0.839	38.40	0.940	91.00	37.00	24.60	108.0	202.0	
		Mean	0.510	13.10	0.246	46.20	17.00	14.80	49.1	122.0	
		SD	0.158	10.10	0.220	23.90	9.01	7.36	23.4	43.0	
		CV (%)	12.300	77.30	89.400	51.70	53.00	49.70	47.7	35.2	
River sediments	12	Min	0.377	2.80	0.170	41.00	10.20	11.40	23.7	94.0	
		Max	0.799	20.00	1.320	94.00	31.50	27.50	64.6	202.0	
		Mean	0.608	7.34	0.623	63.40	17.30	19.70	39.2	143.0	
		SD	0.114	4.39	0.360	16.70	5.51	5.20	12.5	37.1	
		CV (%)	18.700	59.90	57.800	26.30	31.80	26.40	32.0	26.1	
Total	27	Min	0.207	1.40	0.050	4.00	2.50	2.00	21.5	56.0	
		Max	0.839	38.40	1.320	94.00	37.00	27.50	107.5	202.0	
		Mean	0.553	10.50	0.413	53.90	17.10	17.00	44.7	131.0	
		SD	0.146	8.53	0.350	22.60	7.60	6.92	19.8	41.7	
		CV (%)	26.400	80.90	84.600	42.00	44.30	40.70	44.3	31.8	
Urban and suburban soils of Lishui City	126	Min	—	0.93	0.050	9.41	4.72	3.70	29.2	60.0	Wang and Lu, 2011
		Max	—	36.50	1.900	105.10	141.00	50.20	1 673.0	874.0	
		Mean	—	8.81	0.530	34.66	35.75	14.35	63.2	192.4	
		SD	—	5.31	0.520	15.79	21.37	7.26	22.0	133.6	
		CV (%)	—	60.00	72.000	45.70	59.70	50.60	34.8	69.4	
Farmland soils in Changshan County, northwestern Zhejiang Province	1 788	Min	—	1.15	0.040	10.10	7.18	5.61	16.5	24.5	Wang, 2025
		Max	—	688.00	27.100	264.00	615.00	264.00	147.0	1 088.0	
		Mean	—	15.30	0.530	65.90	30.40	29.10	34.0	99.8	
		SD	—	26.40	1.260	20.30	23.70	17.40	11.4	65.9	
		CV (%)	—	172.00	238.000	31.00	78.00	60.00	33.0	66.0	
Farmland soils in Anji County, northwestern Zhejiang Province	169	Min	—	2.82	0.050	20.30	5.75	8.70	20.2	37.9	Cao et al., 2025
		Max	—	114.00	5.050	100.00	92.30	85.00	87.1	300.0	
		Mean	—	17.10	0.748	60.10	26.90	27.70	35.7	105.0	
		SD	—	15.50	0.899	17.80	12.80	11.10	9.3	46.4	
		CV (%)	—	90.30	120.000	29.60	47.60	40.00	26.1	44.1	
GB 15618-2018	—	—	—	40.00	0.300	150.00	50.00	70.00	90.0	200.0	MEEC and SAMR, 2018
Background values of soils in Zhejiang Province	—	—	0.350	9.20	0.070	52.90	17.60	24.60	23.7	70.6	China Environmental Monitoring Center, 1990

a: number of samples; —: no data.

The concentration of Cd, Cu, Pb, and Zn were lower than those reported for urban and suburban soils from Lishui City (Wang and Lu, 2011), which is consistent with the greater influence of

industrialization and urbanization on PTE enrichment in urban areas (Wang and Lu, 2011). Compared with those in cultivated soils in cultivated soils from Songyang County, the mean Cd

(0.310 mg/kg) and Pb (70.3 mg/kg) concentrations were lower, whereas the As concentration (10.5 mg/kg) was notably greater (3.41 mg/kg) (Xu et al., 2021). Compared with those in farmland soils developed from black shale in Changshan (Wang, 2025) and Anji County (Cao et al., 2025), the mean concentrations of As, Cd, Cr, Cu, and Ni in surface soils in this study were lower, which reflects the natural enrichment of these elements in black shale (Wu et al., 2024; Cao et al., 2025; Wang, 2025). However, Pb and Zn concentrations were higher than those in black shale-derived soils, despite the occurrence of Pb and Zn enrichment in shale lithologies (Wu et al., 2024; Cao et al., 2025; Wang, 2025). This contrast suggests that the elevated Pb and Zn levels in the study area are primarily controlled by anthropogenic inputs, which are likely associated with agricultural practices, rural settlements, and atmospheric deposition.

3.2 Spatial distribution characteristics of PTEs in surface soils and river sediments

The spatial distributions of PTEs in surface soils and river sediments are shown in Fig.2. In the surface soils (Fig.2a), Cr, Cu, and Ni exhibited broadly similar patterns, with concentrations generally decreasing from upstream to downstream. The highest Cr (91.0 mg/kg) and Ni (24.6 mg/kg) concentrations occurred at site J10, whereas the Cu concentration peaked at site J27 (37.0 mg/kg). The lowest concentrations of Cr (4.00 mg/kg), Cu (2.50 mg/kg), and Ni (2.00 mg/kg) were recorded at site J3. In contrast, As, Cd, Pb, and Zn exhibited coherent patterns, with high-value zones concentrated in the midstream to downstream reaches. The maximum concentrations of As (38.4 mg/kg), Cd (0.94 mg/kg), and Zn (202 mg/kg) occurred at site J7, whereas Pb reached its peak concentration (108 mg/kg) at site J17.

Overall, the spatial patterns of PTEs in the river sediments closely corresponded to those in the surface soils, indicating that riverine PTEs are largely controlled by inputs from adjacent soils through erosion. Such soil-sediment coupling is supported by the consistent distributions across both matrices. However, a clear dilution effect was observed for As in the river sediments relative to the surface soils, reflecting its higher mobility during transport. In contrast, Cd, Cr, Cu, Ni, Pb, and Zn demonstrated weaker dilution effects, with their concentrations better preserved during fluvial transport. The relatively high levels of these metals

in the upstream and midstream soils, coupled with their increased accumulation in the downstream sediments, highlight their differential behavior during transport and deposition. Notably, the enrichment of PTEs in depositional zones suggests that fluvial processes facilitate downstream accumulation, even where dilution effects reduce concentrations in local soils.

3.3 Risk assessment of PTEs in surface soils and river sediments

Exceedance analysis revealed that the Cd, Cr, Pb, and Zn concentrations surpassed the corresponding background values in Zhejiang soil (Table 1; China Environmental Monitoring Center, 1990) in 88.9%, 55.6%, 92.6%, and 88.9% of the samples, respectively, whereas the concentration of As, Cu, and Ni exceeded the corresponding background values less frequently (<45%). These results indicate that Cd, Pb, and Zn are the primary pollutants of concern in the study area.

The EF results (Fig.3a) highlighted PTE-specific behaviors. Cd exhibited the greatest variation (0.54–12.1), ranging from no enrichment to moderately severe enrichment. The median EF(Cd) values were substantially greater in the river sediments (5.23) than in the surface soils (1.88), reflecting its enhanced mobility and accumulation during fluvial transport. Pb and Zn were slightly enriched, whereas As, Cr, Cu, and Ni were generally not significantly enriched. Previous studies have suggested that $EF \leq 1.5$ indicates that a given PTE is derived primarily from natural sources (Wang et al., 2023b). In the surface soils, the proportions of samples with $EF \leq 1.5$ for As, Cd, Cr, Cu, Ni, Pb, and Zn accounted for 60.0%, 33.3%, 100%, 93.3%, 100%, 53.3%, and 86.7% respectively, of the total samples, indicating that Cr, Cu, and Ni are derived mainly from natural inputs. In the river sediments, only one sample revealed a Cd (EF) value ≤ 1.5 , whereas most of the other PTEs yielded EF values below this threshold. Although As and Pb in soils can be partially attributed to anthropogenic activity, their concentrations in sediments are diluted during erosion and transport, suggesting greater lithogenic control in sediments.

Moreover, I_{geo} provided evidence of anthropogenic influence (Cai et al., 2024; Adnan et al., 2025), with spatial variations illustrated in Fig.3b. Concentrations of As, Cr, Cu, Ni, Pb, and Zn consistently yielded I_{geo} values below 0 in both the surface soils and river sediments, indicating an unpolluted status. In

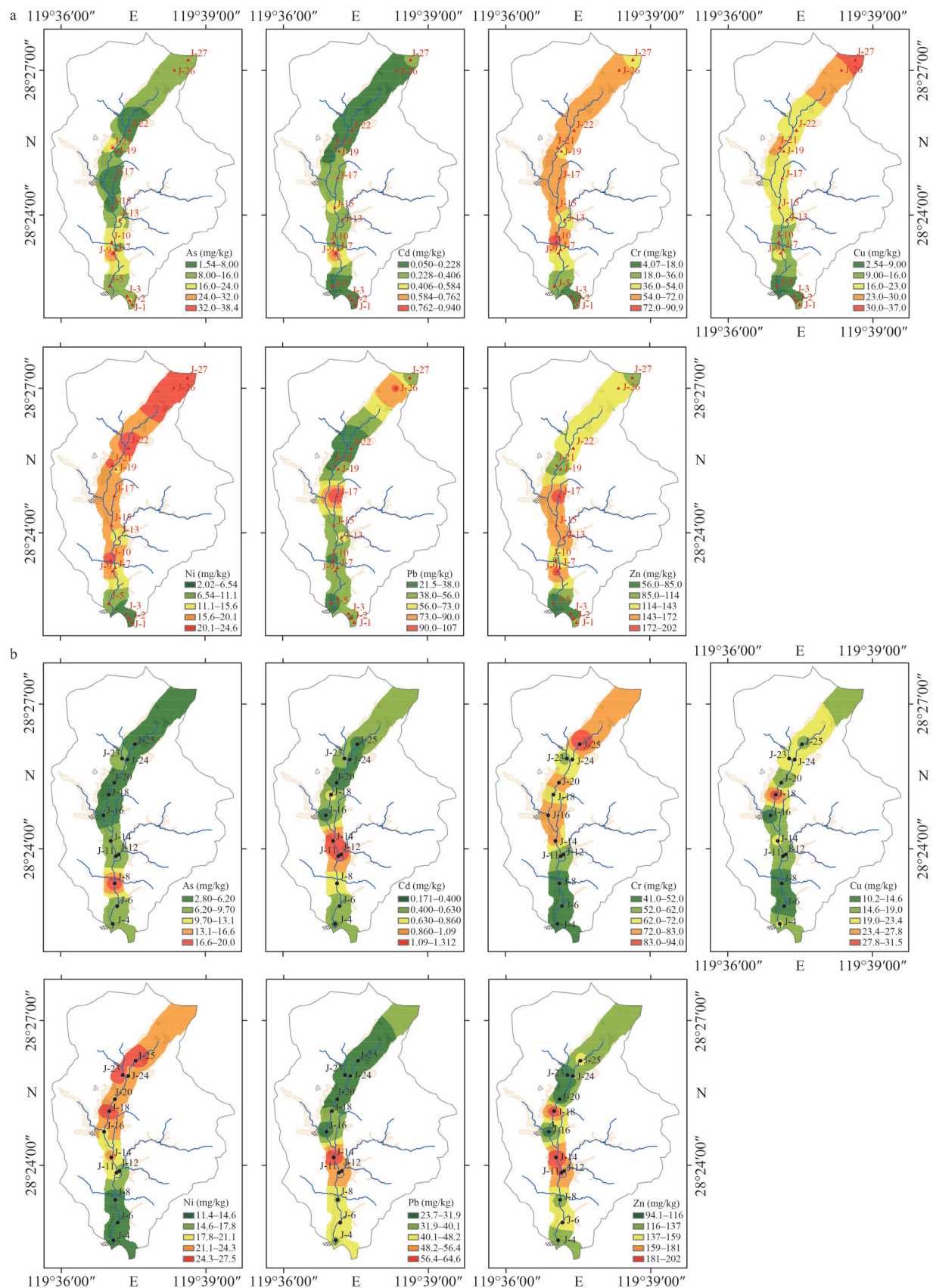


Fig.2 Spatial distribution of the concentrations of PTEs in surface soils (a) and river sediments (b) in the study area

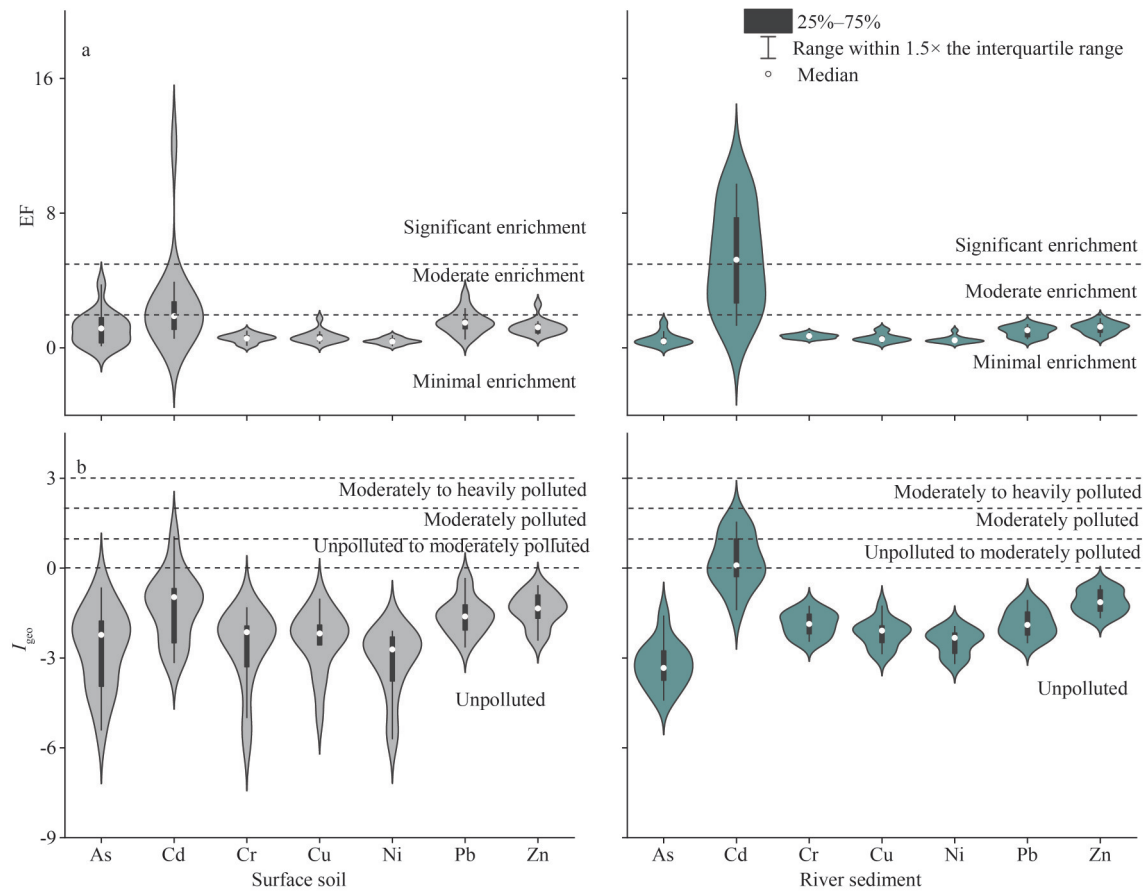


Fig.3 Enrichment factor and geo-accumulation index values of PTEs in the surface soils and river sediments from the study area

contrast, Cd exhibited the most pronounced enrichment. Specifically, 66.7% of the samples were categorized as unpolluted, 18.5% as unpolluted to moderately polluted, and 14.8% as moderately polluted. Notably, the median I_{geo} values for Cd, Cr, Cu, Ni, and Zn were higher in the surface soils than in river sediments. Conversely, As and Pb displayed an opposite pattern. This disparity suggests the preferential retention of Cd within the surface soil matrix, contrasted with the higher mobility and subsequent dilution of As and Pb during their transport from terrestrial to aquatic environments.

The NPI for PTEs results are summarized in Table 2. For surface soils, the NPI values of individual elements ranged from 0.290 (Ni) to 2.29 (Cd). Among the analyzed elements, Cd was the

only one to exhibit a moderate pollution level (Kowalska et al., 2018). Concentrations of Cr, Cu, and Ni remained below 0.7, corresponding to the “Clean” category, while As, Pb, and Zn were classified at the “Warning limit” (Kowalska et al., 2018). The integrated Nemerow pollution index (NPI-total) for the surface soils was 2.24, indicating an overall moderate pollution status. In comparison, river sediments exhibited a higher degree of contamination. Individual NPI values for the river sediments ranged from 0.316 (Ni) to 3.16 (Cd). Notably, Cd reached a heavy pollution level (Kowalska et al., 2018), whereas As, Cr, Cu, Ni, and Pb fell within the “Clean” categories, and Zn remained at the “Warning limit” (Kowalska et al., 2018). The NPI-total for river sediments was 3.15,

Table 2 Nemerow comprehensive pollution index of PTEs in surface soils and river sediments

	As	Cd	Cr	Cu	Ni	Pb	Zn	NPI-total
Surface soil	0.717	2.29	0.481	0.576	0.290	0.928	0.834	2.24
River sediment	0.423	3.16	0.493	0.506	0.316	0.637	0.834	3.15

signifying an overall heavy pollution level (Kowalska et al., 2018). Collectively, these results demonstrate that Cd is the primary driver of PTE pollution in the study area. Furthermore, the higher NPI-total values in the river sediments relative to the surface soils confirm that river sediments act as a more significant sink for PTE accumulation, exhibiting more severe contamination.

The variation in the potential ecological RI for surface soils indicates that, with the exception of sample J7 (RI=112), which corresponds to a moderate ecological risk, all other soil samples fall within the low ecological risk category (RI<65) (Fig.4a, b). In contrast, RI values for river sediments exhibit a much broader range. Sediments from the midstream region show moderate ecological risk at

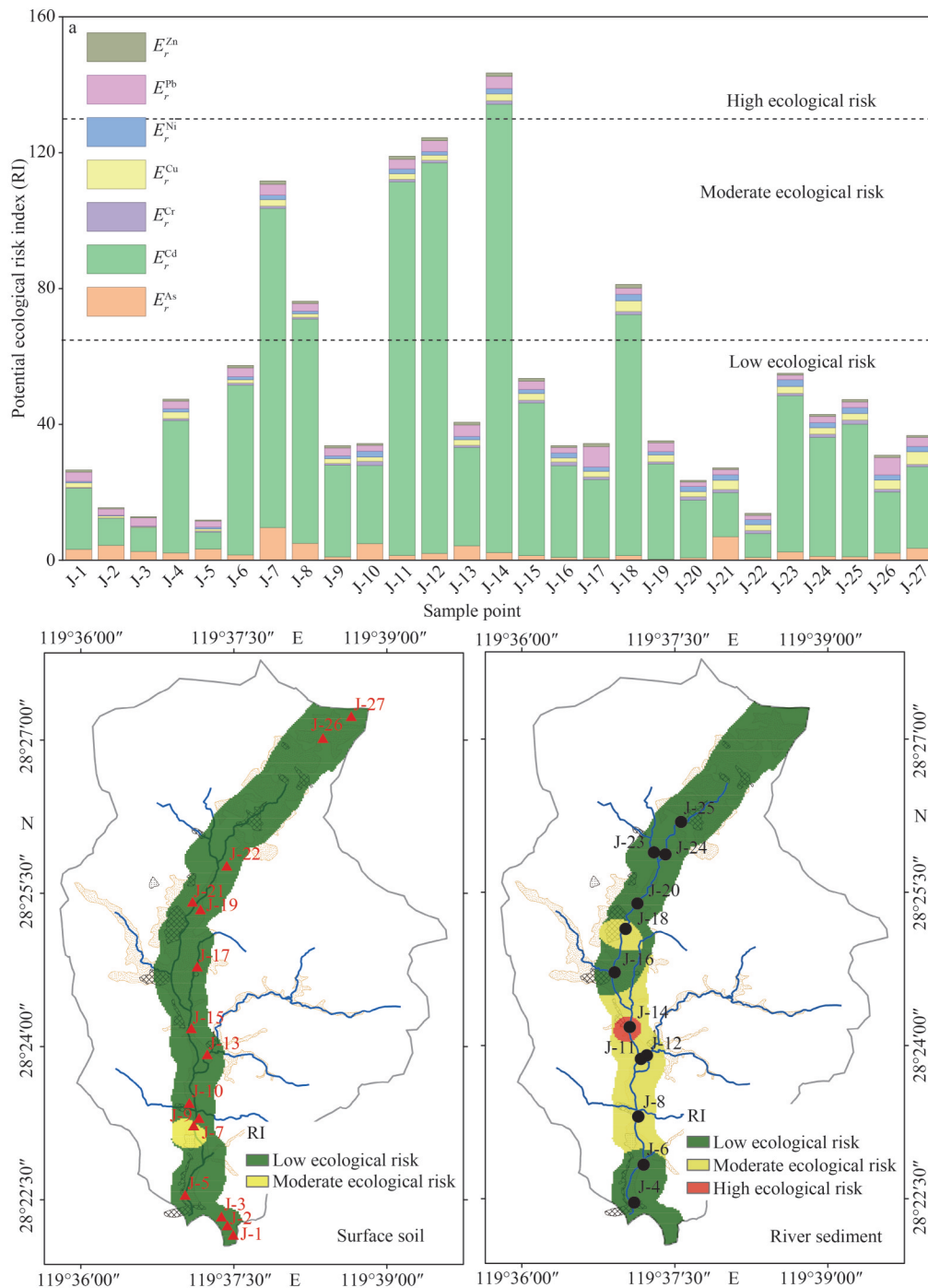


Fig.4 Contribution of individual potentially toxic elements (PTEs) to the potential ecological risk indices (a), and distribution of potential ecological risk indices in the surface soils (b) and river sediments (c) of the study area

sites J8–J12, increasing to high ecological risk at site J14 (RI=143) (Fig.4a, c). River sediments from other areas are generally characterized by low ecological risk, except for site J18, which is classified as moderate ecological risk. Spatially, RI values display pronounced heterogeneity, with elevated ecological risks predominantly concentrated in the middle reaches (sampling sites J7–J15) for both surface soils and river sediments (Fig.4b, c). Notably, RI values in river sediments are consistently higher than those in the corresponding surface soils. This systematic discrepancy suggests progressive enrichment of potentially toxic elements (PTEs) during fluvial transport, leading to an amplification of ecological risk within the aquatic environment. The RI assessment further identifies Cd as the dominant contributor to ecological risk (Fig.4a), accounting for 42.2%–82.5% of the total RI (mean=73.8%). The single-element potential ecological risk (E_r^x) values for other PTEs remain below 40, indicating low ecological risk (Hakanson, 1980). In contrast, E_r^{Cd} values span a wide range (5–132), crossing multiple risk thresholds. Overall, 66.7% of the samples are classified as low ecological risk, 18.5% as moderate ecological risk, and 14.8% as moderate to high ecological risk. In surface soils, E_r^{Cd} values generally indicate low ecological risk, except at site J7 ($E_r^{\text{Cd}}=94$). Conversely, river sediments exhibit substantially higher vulnerability, with only 41.7% of samples categorized as low ecological risk, while 33.3% and 25.0% fall into the moderate and moderate to high ecological risk categories, respectively. These high-risk sediment samples are mainly distributed in the middle reaches (sites J11, J12, and J14). Consistent with the RI patterns, E_r^{Cd} values in river sediments consistently exceed those in adjacent surface soils, reinforcing the inference that Cd preferentially partitions into the sediment phase during its transport through the watershed.

4 DISCUSSION

4.1 Source of PTEs in surface soils

Principal component analysis (PCA) was performed on eight elements (As, Cd, Cr, Cu, Ni, Pb, Zn, and Ti) in the surface soils to discern their potential sources. Prior to analysis, all variables were standardized using Z-score normalization to eliminate dimensional effects. Following the Kaiser criterion (eigenvalues ≥ 1), three principal components (PCs) were extracted, accounting for 84.4% of the total cumulative variance.

This high percentage explained variance indicates that the extracted PCs effectively retained the essential geochemical information of the original dataset.

For surface soils (Supplementary Table S4), PC1 accounted for 39.3% of the total variance and was dominated by Cr (0.937), Ni (0.970), Ti (0.767), and Cu (0.769). This component reflects a predominantly lithogenic source associated with parent material weathering, with minor anthropogenic influence. Ti, commonly regarded as a conservative tracer of natural inputs due to its low mobility and negligible anthropogenic contribution (Zozulya et al., 2022), showed only moderate loading on PC1 and did not form an independent natural factor, suggesting that natural geochemical signals in soils are partly overprinted by human activities.

PC2 explained 23.7% of the variance and was characterized by strong positive loadings of Pb (0.887) and Zn (0.804), a well-established tracer of traffic-related emissions, reflecting the influence of atmospheric deposition (Peng et al., 2019; Wang et al., 2023a; Chen et al., 2024). PC3 accounted for 20.0% of the variance and was primarily loaded by As (0.859) and Cd (0.812), indicating dominant anthropogenic inputs. These elements are commonly associated with agricultural practices (e.g., fertilizers and pesticides) and industrial emissions, consistent with the intensive agricultural land use in the study area.

To further constrain element associations and source characteristics, Spearman correlation analysis and hierarchical cluster analysis (HCA) were conducted (Fig.5a). Strong positive correlations ($r>0.6$, $P\leq 0.05$) were observed among Cr, Ni, and Ti in surface soils, indicating common geochemical controls. Titanium in the study area is mainly derived from granite weathering, where it occurs in biotite through isomorphic substitution and in accessory minerals such as titanite, rutile, and ilmenite (Douce, 1993; Taboada et al., 2006; El-Dokouny et al., 2023). During weathering, Ti is largely immobilized as refractory TiO_2 phases, resulting in residual enrichment in soils (Milnes and Fitzpatrick, 1989; Augustsson et al., 2023). The close association of Cr and Ni with Ti suggests that these elements are also predominantly of lithogenic origin, characterized by low solubility and limited mobility. Copper showed moderate correlations with this group, indicating that granite weathering is likewise its primary source. Cluster analysis supports this interpretation, grouping Cr, Cu, Ni, and Ti into a distinct natural-source cluster, consistent with previous studies in Zhejiang Province (Yang et al., 2021).

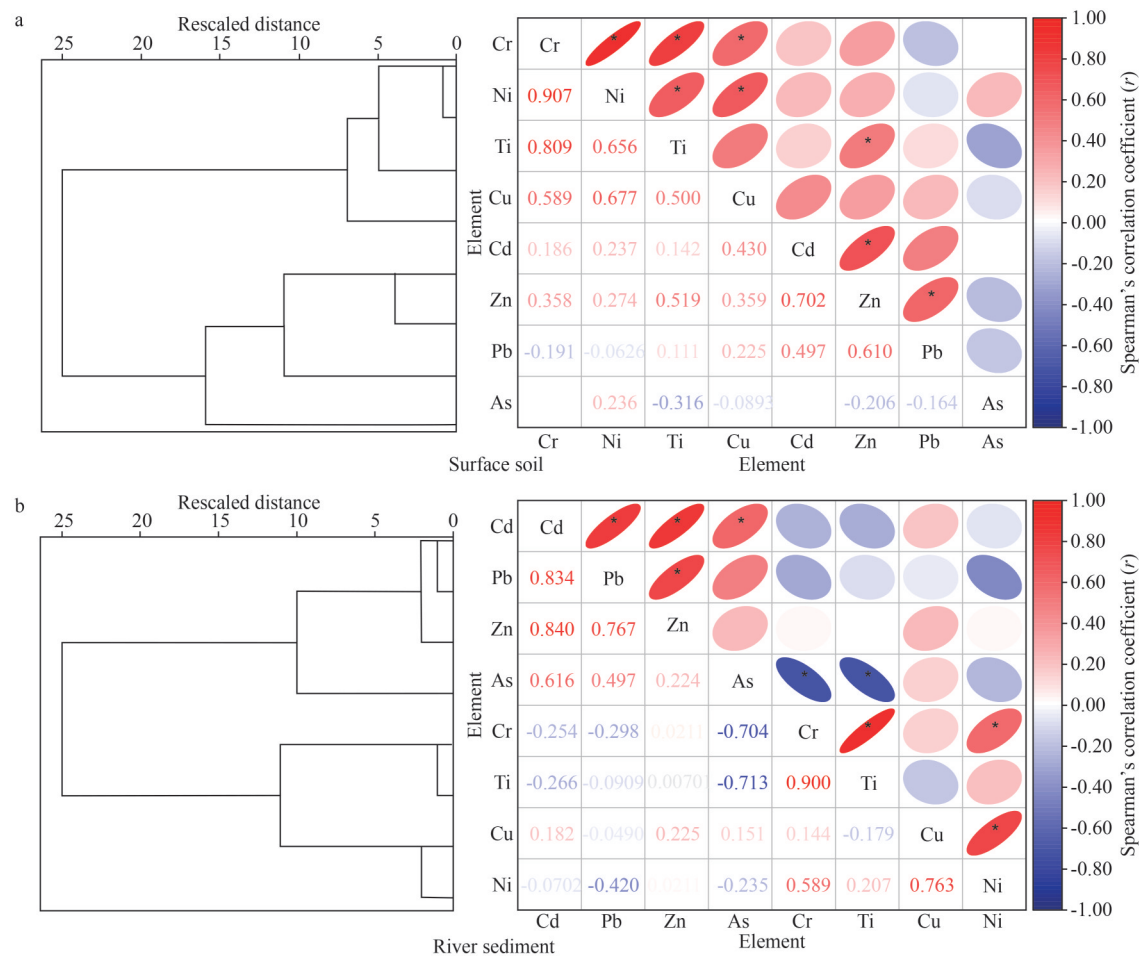


Fig.5 Spearman correlation and hierarchical clustering analyses (Ward's method with squared Euclidean distance for grouping) of potentially toxic elements (PTEs) in the surface soils (a) and river sediments (b) from the study area

An asterisk indicates a significant correlation at $P < 0.05$.

In contrast, Cd and Pb were significant positive correlated with Zn in the surface soils ($r = 0.702$ and 0.610 , respectively; Fig.5a), indicating shared anthropogenic sources. In southeastern China, atmospheric deposition represents a major pathway for Pb, Zn, and Cd accumulation in agricultural soils, contributing approximately 74%, 92%, and 32% of their respective inputs (Peng et al., 2019). Additional inputs arise from livestock manure and chemical fertilizers, particularly phosphate fertilizers, which contain elevated Cd concentrations (Wang and Ma, 2004). The study area is characterized by intensive fertilizer application to support rice and tea cultivation (Yang and Lin, 2020), and previous studies in Songyang County have shown that more than 80% of soil Cd originates from fertilizer use and atmospheric deposition (Xu et al., 2021). Accordingly, elevated Cd, Pb, and Zn concentrations were mainly

observed in the middle and downstream agricultural areas. Hierarchical clustering further grouped Cd, Pb, and Zn into a distinct anthropogenic cluster, confirming that agricultural activities and atmospheric deposition are the dominant sources of these PTEs in surface soils.

4.2 Geochemical behavior of PTEs during river sediment transport

Compared with the surface soils, the source separation of PTEs in the river sediments is more distinct, reflecting the integrative effects of erosion, transport, and deposition within the fluvial system. PCA performed on the standardized dataset of river sediment samples extracted three principal components, explaining 90.80% of the total variance, indicating higher representativeness than that obtained for surface soils.

In the river sediments (Supplementary Table S4),

PC1 accounted for 34.9% of the total variance and was characterized by high loadings of Cd (0.958), Pb (0.928), and Zn (0.930). PC2 explained 29.3% of the variance, dominated by Cr (0.875) and Ti (0.950), while PC3 accounted for 26.6% and was strongly associated with Cu (0.957) and Ni (0.902). These PCA results for the river sediments exhibit a distinct discrepancy from those observed in the surface soils, further suggesting divergent geochemical behaviors and transport mechanisms of these elements during the sedimentation process.

Spearman correlation and hierarchical cluster analyses further support the PCA-based source interpretation (Fig.5b). Strong positive correlations ($r > 0.7$, $P \leq 0.05$) among Cd, Pb, and Zn suggest coherent geochemical behavior and similar particle-associated transport pathways in the river sediments. These elements are known to preferentially associate with fine particles, Fe-Mn oxides, carbonates, and organic matter, rather than silicate minerals, resulting in strong enrichment during erosion and downstream transport (Bordas and Bourg, 2001; Garçon et al., 2014; Peng et al., 2022). Compared with the surface soils, tighter correlations and more coherent clustering patterns in sediments indicate cumulative enrichment of anthropogenic PTEs at the watershed scale.

The geochemical behaviors of PTEs during sediment transport are controlled not only by their sources but also by interfacial processes at the water-sediment boundary, including adsorption, desorption, and precipitation (Wang et al., 1997; Bordas and Bourg, 2001; Li et al., 2022). In contrast to anthropogenic elements, Cr and Ti exhibited a strong positive correlation in the river sediments ($r = 0.900$, $P \leq 0.05$), consistent with a shared lithogenic origin. As a high field strength element with extremely low mobility, Ti is highly resistant to dissolution and transformation and is predominantly retained in insoluble mineral phases during weathering and transport (Augustsson et al., 2023; Bertrand et al., 2024). During fluvial transport, labile elements are preferentially leached, whereas Ti remains enriched in residual fractions, preserving the geochemical signature of the source rock. The close association between Cr and Ti therefore indicates that Cr is also largely controlled by natural weathering processes and exhibits low mobility and high sedimentary stability.

Ni and Cu, although primarily of natural origin in the surface soils, display more complex behaviors in the river sediments due to their variable oxidation

states and affinity for adsorption and complexation (Gao et al., 2021). During transport, these elements preferentially accumulate in fine-grained particles and on the surfaces of clay minerals or Fe-Mn oxides (Miranda et al., 2022). However, their mineral hosts and hydrodynamic sorting differ from those of Ti, which is mainly contained in heavy minerals such as rutile and ilmenite. This contrast in particle size and settling behavior weakens the correlations between Ni, Cu, and Ti in the river sediments and results in greater spatial heterogeneity.

4.3 Soil-sediment transfer and geochemical behavior of PTEs

The results reveal a clear soil to sediment transfer pathway of PTEs within the studied small granite-derived watershed, where the fate of PTEs is governed by a synergy of lithogenic inheritance and anthropogenic forcing. Geogenic elements (Cr, Ni, and Ti) exhibit conservative behavior along the soil-sediment continuum, maintaining stable lithogenic signatures from granite weathering. The immobilization of Ti in resistant mineral phases effectively anchors the natural geochemical baseline, while the low mobility of Cr and Ni reflects their sequestration within silicate lattices with minimal interfacial reactivity.

In contrast, anthropogenic PTEs (Cd, Pb, and Zn) demonstrate pronounced soil-to-sediment fractionation. These elements are mobilized from agricultural soils via runoff and subsequently enriched in sediments through adsorption onto fine-grained fractions, Fe-Mn oxides, and organic matter. The systematically higher EF, NPI, and RI values in sediments relative to soils confirm a progressive downstream enrichment effect, identifying river sediments as a critical sink and amplifier of anthropogenic contamination. Notably, Cd emerges as the primary driver of ecological risk, exhibiting the highest sensitivity to fluvial redistribution and disproportionately influencing the integrated RI.

While the integrated multivariate and index-based approaches offer robust insights, several constraints warrant attention. The current assessment, based on total concentrations, does not account for the bioavailable speciation or geochemical fractions that dictate actual toxicity. Furthermore, the absence of temporal (seasonal) monitoring limits the understanding of PTE dynamics under varying hydrodynamic regimes.

Future investigations should prioritize a multi-dimensional approach to further elucidate the

geochemical dynamics of the watershed. Specifically, integrating chemical speciation analysis (e.g., European Community Bureau of Reference (BCR) sequential extraction) is essential to assess the actual bioavailability and toxicity of PTEs beyond total concentrations. Furthermore, employing high-resolution isotopic tracing (e.g., Pb, Zn, or Cd isotopes) would enable precise quantification of anthropogenic contributions. Finally, incorporating multi-seasonal monitoring and hydrodynamic modeling is necessary to capture the temporal variability and episodic transport of contaminants during varying hydrological regimes. These efforts will refine ecological risk evaluations and facilitate targeted pollution control strategies in granite-hosted agricultural landscapes.

5 CONCLUSION

This study provides a process-based understanding of PTE behavior in a small, granite-derived agricultural watershed by integrating soil-sediment coupling, source apportionment, and ecological risk assessment. The results demonstrate a clear contrast between lithogenic and anthropogenic controls on PTE dynamics. Cr, Cu, Ni, and Ti are primarily governed by granite weathering, exhibiting low mobility and geochemical stability during erosion and fluvial transport. In contrast, Cd, Pb, and Zn are dominated by anthropogenic inputs, mainly agricultural practices and atmospheric deposition, and show strong particle-bound transport and cumulative enrichment in river sediments. Cd is identified as the key ecological risk driver, contributing 42.2%–92.5% (mean 73.8%) of the total potential ecological RI, with midstream sediments acting as hotspots of risk amplification. This highlights the role of fluvial processes in magnifying Cd related risks even under moderate soil contamination. The findings emphasize the river sediments as sensitive indicators of diffuse agricultural pollution and support targeted management strategies, including reducing Cd-rich phosphate fertilizers, optimizing fertilizer application rates, and implementing erosion control measures (e.g., buffer strips and reduced tillage) to mitigate Cd dominated ecological risks in granite-derived agricultural watersheds.

6 DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the author upon reasonable request.

References

- Adnan M, Zhao P, Xiao B H et al. 2025. Heavy metal pollution and source analysis of soils around abandoned Pb/Zn smelting sites: environmental risks and fractionation analysis. *Environmental Technology & Innovation*, **38**: 104084, <https://doi.org/10.1016/j.eti.2025.104084>.
- Augustsson C, Aehnelt M, Olivarius M et al. 2023. Provenance from the geochemical composition of terrestrial clastic deposits—a review with case study from the intracontinental Permo-Triassic of European Pangea. *Sedimentary Geology*, **456**: 106496, <https://doi.org/10.1016/j.sedgeo.2023.106496>.
- Bertrand S, Tjallingii R, Kylander M E et al. 2024. Inorganic geochemistry of lake sediments: a review of analytical techniques and guidelines for data interpretation. *Earth-Science Reviews*, **249**: 104639, <https://doi.org/10.1016/j.earscirev.2023.104639>.
- Bordas F, Bourg A. 2001. Effect of solid/liquid ratio on the remobilization of Cu, Pb, Cd and Zn from polluted river sediment. *Water, Air, and Soil Pollution*, **128**(3): 391–400, <https://doi.org/10.1023/A:1010319004844>.
- Cai N, Wang X P, Wang W L et al. 2024. Accumulation, ecological health risks, and source identification of potentially toxic elements in river sediments of the Qinghai-Tibet Plateau, China. *Process Safety and Environmental Protection*, **182**: 703–718, <https://doi.org/10.1016/j.psep.2023.12.026>.
- Cao M M, Tang Q F, Gai N et al. 2025. Contamination characteristics, source apportionment, and risk assessment of heavy metals and metalloids in the soil-crop-human system within the typical high geological background region of the Yangtze River Delta. *Journal of Environmental Management*, **391**: 126443, <https://doi.org/10.1016/j.jenvman.2025.126443>.
- Chen L, Fang L C, Yang X et al. 2024. Sources and human health risks associated with potentially toxic elements (PTEs) in urban dust: a global perspective. *Environment International*, **187**: 108708, <https://doi.org/10.1016/j.envint.2024.108708>.
- China Environmental Monitoring Center. 1990. Background Values of Soil Elements in China. Beijing: China Environment Science Press, p.329–493. (in Chinese)
- Cui J L, Zhou X Y, Chen Y X et al. 2023. Geochemical enrichment, speciation and mobilization of arsenic and antimony in black shales (southern China): evidence from sequential fractionation and XANES spectroscopy. *Chemical Geology*, **637**: 121647, <https://doi.org/10.1016/j.chemgeo.2023.121647>.
- Douce A E P. 1993. Titanium substitution in biotite: an empirical model with applications to thermometry, O₂ and H₂O barometries, and consequences for biotite stability. *Chemical Geology*, **108**(1–4): 133–162, [https://doi.org/10.1016/0009-2541\(93\)90321-9](https://doi.org/10.1016/0009-2541(93)90321-9).
- Efthimiou N, Psomiadis E, Panagos P. 2020. Fire severity and soil erosion susceptibility mapping using multi-temporal Earth Observation data: the case of Mati fatal wildfire in Eastern Attica, Greece. *Catena*, **187**: 104320, <https://doi.org/10.1016/j.catena.2019.104320>.

- El-Dokouny H A, Mahdy N M, El Hadek H H et al. 2023. Origin of amphibole-biotite-fluorite-rich enclaves from Gabal El-Ineigi fluorite-bearing granite, central eastern desert of Egypt: insights into fluoride-calcium and silicate liquid immiscibility. *Minerals*, **13**(5): 670, <https://doi.org/10.3390/min13050670>.
- Fang P G, Wang Q G, Zhong Q Q et al. 2026. Bioaccumulation and health risk assessment of heavy metals in commercial shellfish from Zhoushan, one of China's largest seafood markets. *Marine Pollution Bulletin*, **223**: 118964, <https://doi.org/10.1016/j.marpolbul.2025.118964>.
- Gao L, Li R, Liang Z B et al. 2021. Mobilization mechanisms and toxicity risk of sediment trace metals (Cu, Zn, Ni, and Pb) based on diffusive gradients in thin films: a case study in the Xizhi River basin, South China. *Journal of Hazardous Materials*, **410**: 124590, <https://doi.org/10.1016/j.jhazmat.2020.124590>.
- Garçon M, Chauvel C, France-Lanord C et al. 2014. Which minerals control the Nd-Hf-Sr-Pb isotopic compositions of river sediments? *Chemical Geology*, **364**: 42-55, <https://doi.org/10.1016/j.chemgeo.2013.11.018>.
- Gong J J, Gao J W, Wu H et al. 2024. Heavy metal spatial distribution, source analysis, and ecological risks in the central hilly area of Hainan Island, China: results from a high-density soil survey. *Environmental Geochemistry and Health*, **46**(6): 210, <https://doi.org/10.1007/s10653-024-02031-1>.
- Gope M, Mastro R E, George J et al. 2018. Tracing source, distribution and health risk of potentially harmful elements (PHEs) in street dust of Durgapur, India. *Ecotoxicology and Environmental Safety*, **154**: 280-293, <https://doi.org/10.1016/j.ecoenv.2018.02.042>.
- Hakanson L. 1980. An ecological risk index for aquatic pollution control. a sedimentological approach. *Water Research*, **14**(8): 975-1001, [https://doi.org/10.1016/0043-1354\(80\)90143-8](https://doi.org/10.1016/0043-1354(80)90143-8).
- Heltai G, Györi Z, Fekete I et al. 2018. Longterm study of transformation of potentially toxic element pollution in soil/water/sediment system by means of fractionation with sequential extraction procedures. *Microchemical Journal*, **136**: 85-93, <https://doi.org/10.1016/j.microc.2017.01.026>.
- Hou Q Y, Yang Z F, Yu T et al. 2020. Impacts of parent material on distributions of potentially toxic elements in soils from Pearl River Delta in South China. *Scientific Reports*, **10**(1): 17394, <https://doi.org/10.1038/s41598-020-74490-2>.
- Khalijian A, Lorestani B, Sobhanardakani S et al. 2022. Ecotoxicological assessment of potentially toxic elements (As, Cd, Ni and V) contamination in the sediments of southern part of Caspian Sea, the case of Khazar Abad, Mazandaran Province, Iran. *Bulletin of Environmental Contamination and Toxicology*, **109**(6): 1142-1149, <https://doi.org/10.1007/s00128-022-03621-4>.
- Kowalska J B, Mazurek R, Gąsiorek M et al. 2018. Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination—a review. *Environmental Geochemistry and Health*, **40**(6): 2395-2420, <https://doi.org/10.1007/s10653-018-0106-z>.
- Li H S, Gu Y G, Liang R Z et al. 2023. Heavy metals in riverine/estuarine sediments from an aquaculture wetland in metropolitan areas, China: characterization, bioavailability and probabilistic ecological risk. *Environmental Pollution*, **324**: 121370, <https://doi.org/10.1016/j.envpol.2023.121370>.
- Li J G, Xie Z Y, Qiu X C et al. 2022. Heavy metal habitat: a novel framework for mapping heavy metal contamination over large-scale catchment with a species distribution model. *Water Research*, **226**: 119310, <https://doi.org/10.1016/j.watres.2022.119310>.
- Li J L, Dai J R, Yang L Y. 2025. Heavy metal enrichment characteristics and synergistic evaluation in soil-crop-human systems of agricultural land with different soil parent materials. *Environmental Geochemistry and Health*, **47**(3): 71, <https://doi.org/10.1007/s10653-025-02382-3>.
- Li W Y, Ma C Q, Liu Y Y et al. 2012. Discovery of the Indosinian aluminum A-type granite in Zhejiang Province and its geological significance. *Science China Earth Sciences*, **55**(1): 13-25, <https://doi.org/10.1007/s11430-011-4351-6>.
- Liu X, Xue Q Q, Tian Y Z et al. 2024. Potential toxic components in size-resolved particles and gas from residential combustion: emission factor and health risk. *Environment International*, **185**: 108551, <https://doi.org/10.1016/j.envint.2024.108551>.
- Müller G. 1969. Index of geoaccumulation in sediments of the Rhine River. *GeoJournal*, **2**(3): 108-118.
- Milnes A R, Fitzpatrick R W. 1989. Titanium and zirconium minerals. In: Dixon J B, Weed S B eds. *Minerals in Soil Environments*. Madison: Soil Science Society of America, p.1131-1205, <https://doi.org/10.2136/sssabookser1.2ed.c23>.
- Ministry of Ecology and Environment of China (MEEC), State Administration for Market Regulation (SAMR). Soil environmental quality: risk control standard for soil contamination of agricultural land: GB 15618-2018. Beijing: China Environmental Press, 2018. (in Chinese)
- Miranda L S, Ayoko G A, Egodawatta P et al. 2022. Adsorption-desorption behavior of heavy metals in aquatic environments: influence of sediment, water and metal ionic properties. *Journal of Hazardous Materials*, **421**: 126743, <https://doi.org/10.1016/j.jhazmat.2021.126743>.
- Nie Z Q, Luo J B, Tang J et al. 2025. Pollution sources, characteristics and environmental risk assessment of heavy metals in surface water and sediments of typical pyrite mine in Southwest China. *Journal of Environmental Sciences*, **157**: 742-755, <https://doi.org/10.1016/j.jes.2025.01.008>.
- Ou S H, Sun J, Hu F et al. 2025. Source-oriented and bioaccessibility-based health risk of persistent toxic elements in peri-urban vegetable farm soils of a megacity. *Environmental Chemistry and Ecotoxicology*, **7**: 2005-2006, <https://doi.org/10.1016/j.eneco.2025.09.001>.
- Peng B, Chen H S, Fang X H et al. 2022. Distribution of Pb isotopes in different chemical fractions in bed sediments from lower reaches of the Xiangjiang River, Hunan

- province of China. *Science of the Total Environment*, **829**: 154394, <https://doi.org/10.1016/j.scitotenv.2022.154394>.
- Peng H, Chen Y L, Weng L P et al. 2019. Comparisons of heavy metal input inventory in agricultural soils in North and South China: a review. *Science of the Total Environment*, **660**: 776-786, <https://doi.org/10.1016/j.scitotenv.2019.01.066>.
- Rubinos D A, Jerez Ó, Forghani G et al. 2021. Geochemical stability of potentially toxic elements in porphyry copper-mine tailings from Chile as linked to ecological and human health risks assessment. *Environmental Science and Pollution Research*, **28**(41): 57499-57529, <https://doi.org/10.1007/s11356-021-12844-7>.
- Sakan S, Mihajlidi-Zelić A, Ašković K et al. 2023. The significance of applying different factors for the evaluation of sediment contamination by toxic elements and estimation of the ecological risk. *Environmental Science and Pollution Research*, **30**(18): 53461-53477, <https://doi.org/10.1007/s11356-023-26111-4>.
- Saleh A, Dawood Y H, Gad A. 2022. Assessment of potentially toxic elements' contamination in the soil of Greater Cairo, Egypt using geochemical and magnetic attributes. *Land*, **11**(3): 319, <https://doi.org/10.3390/land11030319>.
- Selahvarzi S, Ardakani S S. 2022. Analysis and health risk assessment of toxic (Cd and Pb) and essential (Cu and Zn) elements through consumption of potato (*Solanum tuberosum*) cultivated in Iran. *International Journal of Environmental Analytical Chemistry*, **102**(18): 6310-6320, <https://doi.org/10.1080/03067319.2020.1807974>.
- Sheng W K, Hou Q Y, Yang Z F et al. 2025. Spatial heterogeneity of Soil Cd and Pb driven by combined effects of pedogenesis and anthropogenic activities: a case study in the mountainous and hilly region of Fujian Province, China. *Environmental Research*, **285**: 122251, <https://doi.org/10.1016/j.envres.2025.122251>.
- Sobhanardakani S. 2017. Potential health risk assessment of heavy metals via consumption of caviar of Persian sturgeon. *Marine Pollution Bulletin*, **123**(1-2): 34-38, <https://doi.org/10.1016/j.marpolbul.2017.09.033>.
- Sreelesh R, Rani G V A, Sreelash K et al. 2025. Seasonal dynamics, sources, and health risks of trace and heavy metals in the tropical critical zone of the Western Ghats, India. *Environmental Geochemistry and Health*, **47**(9): 349, <https://doi.org/10.1007/s10653-025-02658-8>.
- Taboada T, Cortizas A M, García C et al. 2006. Particle-size fractionation of titanium and zirconium during weathering and pedogenesis of granitic rocks in NW Spain. *Geoderma*, **131**(1-2): 218-236, <https://doi.org/10.1016/j.geoderma.2005.03.025>.
- Tepanosyan G, Poghosyan Z, Sahakyan L. 2024. Geochemical characterization of changes in the chemical composition of river sediments under the continuous anthropogenic influence of Yerevan, Armenia. *Environmental Pollution*, **359**: 124553, <https://doi.org/10.1016/j.envpol.2024.124553>.
- Terzano R, Rascio I, Allegretta I et al. 2021. Fire effects on the distribution and bioavailability of potentially toxic elements (PTEs) in agricultural soils. *Chemosphere*, **281**: 130752, <https://doi.org/10.1016/j.chemosphere.2021.130752>.
- Wang F L, Yu Z H, Zhang Y L et al. 2024. Source-risk and uncertainty assessment of trace metals in surface sediments of a human-dominated seaward catchment in eastern China. *Journal of Hazardous Materials*, **480**: 135960, <https://doi.org/10.1016/j.jhazmat.2024.135960>.
- Wang F Y, Chen J S, Chen J L et al. 1997. Surface properties of natural aquatic sediments. *Water Research*, **31**(7): 1796-1800, [https://doi.org/10.1016/S0043-1354\(97\)00013-4](https://doi.org/10.1016/S0043-1354(97)00013-4).
- Wang H Y, Lu S G. 2011. Spatial distribution, source identification and affecting factors of heavy metals contamination in urban-suburban soils of Lishui city, China. *Environmental Earth Sciences*, **64**(7): 1921-1929, <https://doi.org/10.1007/s12665-011-1005-0>.
- Wang M H. 2025. Assessment of heavy metal pollution sources and environmental capacity of typical farmland soils in northwestern Zhejiang based on the geological background of black rock series. *Frontiers in Environmental Science*, **13**: 1601205, <https://doi.org/10.3389/fenvs.2025.1601205>.
- Wang Q C, Ma Z W. 2004. Heavy metals in chemical fertilizer and environmental risks. *Journal of Ecology and Rural Environment*, **20**(2): 62-64, <https://doi.org/10.3969/j.issn.1673-4831.2004.02.015>. (in Chinese with English abstract)
- Wang Q G, Wang H, Ma Y J et al. 2023a. Geochemical distributions of natural radionuclides in surface soils and sediments impacted by lead-zinc mining activity. *Ecotoxicology and Environmental Safety*, **263**: 115210, <https://doi.org/10.1016/j.ecoenv.2023.115210>.
- Wang Q G, Wang J L, Zhong Q Q et al. 2023b. Trace elements accumulation over a century in sediment cores from a tectonic lake on the Qinghai-Tibet plateau: source identification and risk assessment. *Journal of Environmental Management*, **329**: 117030, <https://doi.org/10.1016/j.jenvman.2022.117030>.
- Wei W, Ling S X, Wu X Y et al. 2023. Geochemical accumulation and source tracing of heavy metals in arable soils from a black shale catchment, southwestern China. *Science of the Total Environment*, **857**: 159467, <https://doi.org/10.1016/j.scitotenv.2022.159467>.
- Wu C, Sun B B, Tian M et al. 2024. Enrichment characteristics and ecological risk assessment of heavy metals in a farmland system with high geochemical Background in the Black Shale Region of Zhejiang, China. *Minerals*, **14**(4): 375, <https://doi.org/10.3390/min14040375>.
- Xu H Z, Wu D T, Li G S et al. 2021. Input and output balance of cadmium (Cd) in cultivated land with moderate pollution in Songyang County. *Journal of Zhejiang A&F University*, **38**(6): 1231-1237, <https://doi.org/10.11833/j.issn.2095-0756.20200728>. (in Chinese with English abstract)
- Yan C, Wu Q R, Li R et al. 2025. Enrichment features, ecological risks assessment and quantitative sources appointment of sediment heavy metals: an example of the urbanized Xizhi River catchment, South China.

- Environmental Chemistry and Ecotoxicology*, **7**: 263-274, <https://doi.org/10.1016/j.enceco.2025.01.002>.
- Yang H R, Wang F E, Yu J et al. 2021. An improved weighted index for the assessment of heavy metal pollution in soils in Zhejiang, China. *Environmental Research*, **192**: 110246, <https://doi.org/10.1016/j.envres.2020.110246>.
- Yang J, Han Z Y, Yan Y X et al. 2024. Neglected pathways of heavy metal input into agricultural soil: water-land migration of heavy metals due to flooding events. *Water Research*, **267**: 122469, <https://doi.org/10.1016/j.watres.2024.122469>.
- Yang J H, Lin Y B. 2020. Driving factors of total-factor substitution efficiency of chemical fertilizer input and related environmental regulation policy: a case study of Zhejiang Province. *Environmental Pollution*, **263**: 114541, <https://doi.org/10.1016/j.envpol.2020.114541>.
- Yang S H, Wu Y H, Ma J et al. 2022. Human health risk-based Generic Assessment Criteria for agricultural soil in Jiangsu and Zhejiang provinces, China. *Environmental Research*, **206**: 112277, <https://doi.org/10.1016/j.envres.2021.112277>.
- Ye T C, Liu T C, Yi H L et al. 2025. *In situ* arsenic immobilization by natural iron (oxyhydr) oxide precipitates in As-contaminated groundwater irrigation canals. *Journal of Environmental Sciences*, **153**: 143-157, <https://doi.org/10.1016/j.jes.2024.04.005>.
- Zhang F, Chen Y, Wang W W et al. 2022. Impact of land-use/land-cover and landscape pattern on seasonal in-stream water quality in small watersheds. *Journal of Cleaner Production*, **357**: 131907, <https://doi.org/10.1016/j.jclepro.2022.131907>.
- Zhou Y, Jiang D D, Ding D et al. 2022. Ecological-health risks assessment and source apportionment of heavy metals in agricultural soils around a super-sized lead-zinc smelter with a long production history, in China. *Environmental Pollution*, **307**: 119487, <https://doi.org/10.1016/j.envpol.2022.119487>.
- Zozulya D, Macdonald R, Bagiński B et al. 2022. Nb/Ta, Zr/Hf and REE fractionation in exotic pegmatite from the Keivy province, NW Russia, with implications for rare-metal mineralization in alkali feldspar granite systems. *Ore Geology Reviews*, **143**: 104779, <https://doi.org/10.1016/j.oregeorev.2022.104779>.

Electronic supplementary material

Supplementary material (Supplementary Tables S1–S4) is available in the online version of this article at <https://doi.org/10.1007/s00343-026-5446-4>.