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SEDIMENTS, SEC 1 • SEDIMENT QUALITY AND IMPACT ASSESSMENT • RESEARCH ARTICLE

# Temporal and spatial accumulation of potentially toxic elements (PTEs) in stream sediments from a large lead–zinc mine concentration area of Baoshan, Southwest China

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## Abstract

**Purpose** The aims of this study were to investigate the status, spatial distribution, ecological risk, sources, and temporal accumulation of potentially toxic elements (PTEs) in stream sediments of the Hetaoping large lead–zinc polymetallic mine concentration area.

**Methods** In this study, 35 new collected (2017) and 12 achieved (the 1980s) stream sediments from the Hetaoping and Heiyanao stream drainages in the mine area were used. The geo-accumulation ($I_{geo}$), potential ecological risk ($E_r^i$ and PERI), sediment quality guidelines (SQGs), and mean probable effect concentration quotient (PECQ) were used to evaluate the status and ecological risk of PTEs. Correlation analysis, hierarchical clustering analysis, and enrichment factors (EF) were used to identify the potential source of PTEs. Kruskal–Wallis tests were analyzed to compare the significant difference of PTMs in different drainages and sampling periods.

**Results and discussion** Results showed that As, Cu, Hg, Pb, and Zn are obviously above their regional background values. As, Cd, Cu, Hg, Pb, and Zn are found at moderately contaminated to extremely contaminated levels near the Hetaoping and Maozhupeng deposits, as well as in the Heiyanao drainage. The ecological risk of As, Cd, Hg, and Pb is predominantly near the mining center. Cr and Ni are from natural sources; As, Cd, Cu, Pb, and Zn come from mining activities near the mining center, as well as natural sources outside the mining center, while Hg originates from other uncertain anthropogenic sources.

**Conclusions** Mining activities in the past 40 years have significantly increased As, Cd, Cu, Hg, Pb, and Zn concentrations and ecological risks in the surrounding stream sediments in the study area.

**Keywords** Stream sediments · Lead–zinc mine · PTE contamination assessment · Ecological risk · Potential source identification

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## 1 Introduction

Public concern about potentially toxic elements (PTEs) such as As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn, in soils and sediments, has become a key issue due to rapid industrialization, urbanization, and the rapid economic development in China and worldwide over the past decades (Meybeck et al. 2005; Chen et al. 2008; Yang et al. 2009; Zhang et al. 2010; Arifin et al. 2012; Liu et al. 2012; Brumbaugh et al. 2013; Xiao et al. 2015; Zhuang and Gao 2015; Xu et al. 2020; Li et al. 2021). These elements have long-term toxicity to plants, animals, and humans due to their extensive dissemination, extreme toxicity, and persistence in the environment

(Singh et al. 2005; Nabulo et al. 2010; Dong et al. 2011; Birch and Apostolatos 2013; Shakeri et al. 2020; Zhang et al. 2022). PTEs can originate from either natural or anthropogenic sources. Naturally, they are elevated as a result of the weathering of parent materials which contain considerable levels of PTEs (Becquer et al. 2006; Goldhaber et al. 2009; Antibachi et al. 2012; Tashakor et al. 2014; Zhang et al. 2020a, b). Anthropogenically, they are elevated by agricultural activities, mining operations, industrial discharge, domestic sewage, and fossil fuel combustion (Lu and Li 2006; Goldhaber et al. 2009; McGrath and Tunney 2010; Hamzeh et al. 2011; Addo et al. 2012; Huang et al. 2015; Ke et al. 2015; Zhuang and Gao 2015; Yousefi et al. 2017; Ayari et al. 2021, 2022).

The contamination of aquatic environments by PTEs poses a risk to the natural ecosystem (Lu and Li 2006; Meybeck et al. 2007; Arifin et al. 2012; Qu et al. 2012; Brumbaugh et al. 2013; Cardoso-Silva et al. 2016; Shakeri et al. 2020). Generally, PTEs can be found in a variety of forms in aquatic environments, including adsorption by colloids, suspended matter, water-soluble species, and sedimentary phases (Singh et al. 2005; Rahman et al. 2014; Suresh et al. 2015). Stream sediments play an essential role in PTE contamination in aquatic environments because of their reserve capacity to hold > 90% of metals present (Zahra et al. 2014; Pereira et al. 2015; Shakeri et al. 2020). However, some of the sediment-bound metals may remobilize and be released back into the water and consequently have adverse effects on living organisms when physicochemical conditions such as pH and redox potential of the water system change (Caccia et al. 2003; Dural et al. 2007). Under these conditions, sediments are a potential secondary contamination source for aquatic systems. The temporal and spatial accumulation and distribution characteristics of PTEs in stream sediments can reflect the contamination history of water bodies and have been widely used as a record to understand the risk of PTEs, as well as their natural accumulation and anthropogenic impacts on aquatic environments (Birch et al. 1996; Pekey 2006; Meybeck et al. 2007; Xue et al. 2007; Brumbaugh et al. 2013).

The Hetaoping large lead–zinc polymetallic mine concentration area located north of Baoshan City, Yunnan Province, Southwest China, was first preliminarily delineated in the early 1980s by geochemical anomalies in stream sediments during the Regional Geochemistry-National Reconnaissance Program (RGNR) in China, followed by much detailed investigation and exploration work. Since the late 1990s, large-scale mining activities have begun in parts of these mineral deposits and are ongoing (Li 2011). Previous work, which was based on the RGNR datasets mainly to study regional soil and river sediment geochemical characteristics, has shown elevated PTE (e.g., As, Hg, Cd, Pb, and Zn) concentrations in stream sediments of the Hetaoping large lead–zinc polymetallic mine concentration area (Zhang et al. 2020a). However, the spatial distribution and concentration of PTEs, along with the main drainage system of the mining area, and ecological risk after nearly 40 years of mining and activities, and the potential sources of PTEs are still unclear. These unascertained issues are of great importance to ensure the ecological safety of aquatic environments in the river basin and its future development trends, as well as remediation.

To achieve these goals, this study aims to (1) investigate the concentration and spatial distribution of PTEs in stream sediments of two-stream drainages; (2) evaluate the PTE contamination levels and ecological risk; (3) identify the potential source of these PTEs; (4) analyze the temporal accumulation of PTEs after 40 years of mining activities.

## 2 Materials and methods

### 2.1 Study area and sampling

Baoshan is located in western Yunnan Province, Southwest China (Fig. 1a). The region has complicated topography and moderate elevation and is tempered by a mild subtropical climate with short, mild, dry winters and warm, and wet summers (Zhang et al. 2021). Geologically, Baoshan is located in the Sanjiang area, which consists of the Tengchong, Baoshan, and Lanping-Simao blocks (Wang et al. 2010; Dong et al. 2013; Li et al. 2015). The rock types of the Baoshan Block are mainly Paleozoic to Mesozoic sedimentary rocks, and early Paleozoic and late Mesozoic–early Cenozoic magmatic rocks (Dong et al. 2013; Wang et al. 2013). Mineral deposits, which often lead to PTE pollution in soil and stream sediment, are widely distributed across the Baoshan area (Fig. 1b, Zhang et al. 2020a). The Hetaoping large lead–zinc polymetallic mine concentration area is located 40 km north of the city center of Baoshan. The main deposits of the mine concentration area are the Hetaoping copper-lead–zinc deposit, Maozhupeng lead–zinc deposit, Dachangao iron-gold-lead–zinc polymetallic deposit, Heiyanao lead–zinc polymetallic deposit, Jinchanghe iron-copper-lead–zinc polymetallic deposit, Huangjiadi gold deposit, etc. The Hetaoping lead–zinc deposit is the only large-scale deposit developed in the concentration area. The strata in the concentration area were mainly upper Cambrian strata. Their lithologies are mainly limestone, calcareous slate, and dolomitic marble. Dolomitic marble, hydrothermally altered limestone, and skarn are the main ore-rich rock series of lead–zinc polymetallic ore bodies (Han 2010; Li 2011; Jin 2012; Zhang 2012). A simplified geological map of the Hetaoping large lead–zinc polymetallic mine concentration area is shown in Fig. 1c (modified from Chen 2018).

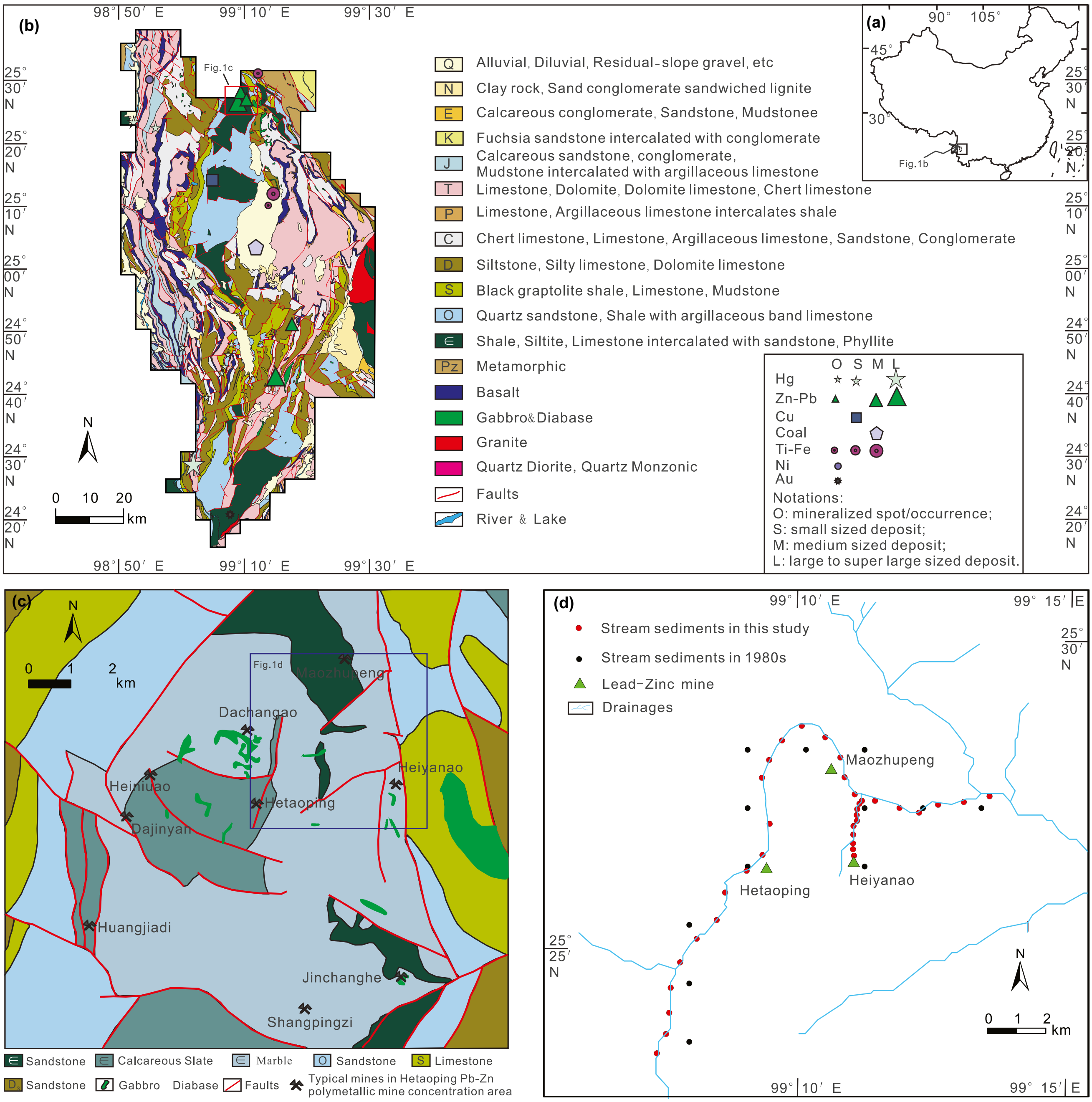


**Fig. 1** General situation of the study area and sample locations. **a** Location of the study area in China; **b** simplified geological and mineral deposit map of the study area (Zhang et al. 2020a); **c** simplified geological map of the Hetaoping Pb–Zn polymetallic mine concentration area, modified from (Chen 2018); **d** stream sediment sample locations in this study and the 1980s

A total of 35 stream sediment samples were collected from the main drainages of the Hetaoping and Heiyanao lead–zinc deposits of the Hetaoping large lead–zinc polymetallic mine concentration area in 2017. With a density of one sample per 500–800 m, 25 samples were collected along the mainstream drainage of the Hetaoping deposit from the upper reaches via the Hetaoping deposit and Maozhupeng deposit to the junction with another streaming system; with a density of one sample per 200 m, 10 samples were collected along the stream drainage of the Heiyanao deposit to the junction with the Hetaoping stream drainage. According to field observations, the Hetaoping deposit drainage is a perennial water gully drainage with a 3 ~ 15 m waterline, while the waterline width of the Heiyanao drainage is usually less than 3 m. All the sample weights were > 500 g, and all the sampling positions were located by a global positioning system (GPS). The stream samples were sampled with 60 mesh (< 0.42 mm) in the field and were further processed to 200 mesh (< 0.074 mm) for analysis (CGS 2006). For comparison, the stream sediment datasets for these two drainages within the sampling distribution range were extracted from the RGNR program of the 1980s and reused. The sample locations in these two periods are shown in Fig. 1d.

## 2.2 Chemical analysis and quality control

Stream sediments were analyzed for total content by ICP–OES (Ni and Cr) and ICP–MS (Cd, Cu, Pb, and Zn), after digestion by hydrofluoric acid (HF), hydrochloric acid (HCl), nitric acid ($HNO_3$), and perchloric acid ($HClO_4$); by AFS (As and Hg) after digestion with aqua regia; and by XRF (Zr) after powder pressing. Analyses were completed at the Hubei Geological Research Laboratory. The analytical methods, brands and models of analytical devices, and detection limits are listed in Table 1. Internal controls were implemented during a routine operation to check the analysis accuracy and precision of the analysis. Briefly, national certified reference materials (CRMs) and laboratory replicate samples were analyzed simultaneously with samples to control the quality of sample analysis. The accuracy was monitored by inserting four CRMs within samples and analyzing them simultaneously. Five samples were selected randomly and re-analyzed by the most experienced analysts in the laboratory to monitor the analysis precision. The accuracies and precisions requirements are listed in Table 2. The pass percent of CRMs and laboratory replicate samples for all analysis indicators in this study are 100%. The accuracies and precisions of all elements in all samples satisfy the analytical requirements of the standard of methods for the analysis of regional geochemical samples (DZ/T 0279 2016) (MLR 2016).

**Table 2** Allowance of accuracy and precision for routine analysis

| Concentration range | Accuracy | Precision |
|---|---|---|
| | $\Delta \lg\overline{C_i} = \lvert \lg\overline{C_i} - \lg C_s \rvert$ | $RD = \lvert C_1 - C_2 \rvert / \frac{1}{2}(C_1 + C_2)$ |
| < 3 detection limit | ≤ 0.17 | ≤ 50% |
| > 3 detection limit | ≤ 0.15 | |
| 1–5% | ≤ 0.10 | |
| > 5% | ≤ 0.15 | |

*CRMs* national certified reference materials, $\overline{C_i}$ the average determined value of $CRM_i$, $C_i$ the determined value of $CRM_i$, $C_s$, the recommended value of $CRM_i$, $C_1$ the first determined value, $C_2$, the re-determined value

## 2.3 Data analysis and mapping

### 2.3.1 Enrichment factor (EF)

The enrichment factor (EF) is widely used to determine the contamination levels of PTEs in sediments and the effects of anthropogenic activities (Li et al. 2012; Dou et al. 2013; Shakeri et al. 2020; Williams and Antoine 2020). The EF is calculated based on Eq. (1).

$$EF = \frac{(C_i/C_r)_{\text{sediment}}}{(C_i/C_r)_{\text{background}}} \tag{1}$$

where "sediment" denotes the studied stream sediments, "background" denotes reference the background, "$C_i$" is the concentration of the selected PTE, and "$C_r$" is the concentration of the reference element. Zirconium is the reference element given its uniformity in these two drainages and its effective use in prior studies (Reimann and Caritat 2005; Zhang et al. 2020a). When $0.5 \leq EF < 1.5$, the element is derived mainly from natural sources, whereas $EF \geq 1.5$ indicates anthropogenic sources (Zhao et al. 2016). An $EF < 2$

**Table 1** The analytical methods, brands and models of the analytical devices and their detection limits

| Indicator | Analytical method | Brand and model of analytical device | Detection limit | Unit |
|---|---|---|---|---|
| As | AFS | Jitian; AFS-820 | 0.2 | mg kg$^{-1}$ |
| Cd | ICP–MS | ThermoFisher; X2 | 0.02 | mg kg$^{-1}$ |
| Cr | ICP–OES | ThermoFisher; iCAP6300 | 1.5 | mg kg$^{-1}$ |
| Cu | ICP–MS | ThermoFisher; X2 | 0.1 | mg kg$^{-1}$ |
| Hg | AFS | Jitian; AFS-820 | 0.0005 | mg kg$^{-1}$ |
| Ni | ICP–OES | ThermoFisher; iCAP6300 | 0.2 | mg kg$^{-1}$ |
| Pb | ICP–MS | ThermoFisher; X2 | 0.2 | mg kg$^{-1}$ |
| Zn | ICP–MS | ThermoFisher; X2 | 1 | mg kg$^{-1}$ |
| Zr | XRF | Shimadzu; XRF-1800X | 1.5 | mg kg$^{-1}$ |

*AFS* cold vapor-atomic fluorescence spectrometry, *ICP–MS* inductively coupled plasma mass spectrometry, *ICP–OES* inductively coupled plasma optical emission spectroscopy, *XRF* X-ray fluorescence spectrometry indicates depletion to minimal contamination; 2 ≤ EF < 5, moderate contamination; 5 ≤ EF < 20, significant contamination; 20 ≤ EF < 40, very strong contamination; and EF ≥ 40, extreme contamination, according to the classification (Barbieri 2016).

#### 2.3.2 Geo-accumulation index (Igeo)

Similarly, the geo-accumulation index ($I_{geo}$) is widely employed to evaluate the contamination levels of PTEs in sediments (Hillman et al. 2015; Chaudhary et al. 2013; Ke et al. 2017; Barbieri et al. 2018; Williams and Antoine 2020; Xu et al. 2020). The $I_{geo}$ was calculated based on Eq. (2).

$$I_{geo} = log2[\frac{C_i}{1.5C_b}] \tag{2}$$

where "$C_i$" is the concentration of selected PTE in stream sediment and "$C_b$" is the background level of that PTE (Müller 1969). $I_{geo} \leq 0$ indicates uncontaminated; $0 < I_{geo} \leq 1$, slightly contaminated; $1 < I_{geo} \leq 2$, moderately contaminated; $2 < I_{geo} \leq 3$, moderately to highly contaminated; $3 < I_{geo} \leq 4$, highly contaminated; $4 < I_{geo} \leq 5$, highly to extremely contaminated; $I_{geo} > 5$, extremely contaminated (Müller 1969).

#### 2.3.3 Potential ecological risk index (PERI)

The potential ecological risk index (PERI) is used to assess the comprehensive potential ecological risk of PTEs in sediment (Hakanson 1980) and is widely used in environmental studies (Ke et al. 2017; Williams and Antoine 2020; Xu et al. 2020). PERI is calculated by Eqs. (3), (4), and (5).

$$C_f^i = \frac{C_s^i}{C_b^i} \tag{3}$$

$$E_r^i = T_r^i \times C_f \tag{4}$$

$$PERI = \sum E_r^i \tag{5}$$

where "$C_f^i$" is the contamination factor, "$C_s^i$" denotes the concentration of selected the PTE in stream sediment and "$C_b^i$" denotes the selected PTE concentration in the reference background. $E_r^i$ is the potential ecological risk of a given PTE and $T_r^i$ is the toxic response factor of a given PTE, calculated using Hg = 40, Cd = 30, As = 10, Pb = 5, Cu = 5, Ni = 5, Cr = 2, and Zn = 1 (Hakanson 1980). The classification of $E_r^i$ is as follows: $E_r^i < 40$, low potential ecological risk; $40 \leq E_r^i < 80$, moderate potential ecological risk; $80 \leq E_r^i < 160$, considerable potential ecological risk; $160 \leq E_r^i < 320$, high potential ecological risk; $E_r^i \geq 320$, very high potential ecological risk (Hakanson 1980). The classification of PERI is as follows: PERI < 150, low potential ecological risk; 150 ≤ PERI < 300, moderate potential ecological risk; 300 ≤ PERI < 600, considerable potential ecological risk; 600 ≤ PERI < 1200, high potential ecological risk; PERI ≥ 1200, very high potential ecological risk (Hakanson 1980).

#### 2.3.4 Sediment quality guidelines (SQGs) and mean probable effect concentration quotient (PECQ)

Sediment quality guidelines (SQGs) provide threshold effect concentrations (TECs) and probable effect concentrations (PECs), which are effective tools for assessing sediment quality conditions in freshwater ecosystems (MacDonald et al. 2000). Levels < TEC indicate a minimal effect, where biological effects are rarely observed; TEC < levels < PEC represent the possible occurrence of biological effects. Levels > PEC indicate a probable effect, where the adverse biological effect frequently occurs.

The mean probable effect levels quotient (PECQ) is used to evaluate the combined effects of multiple contaminants in sediment and calculated by Eq. (6) (MacDonald et al. 2000).

$$PECQ = \frac{\sum_{i=1}^{n} C_i/PEC_i}{n} \tag{6}$$

where "$C_i$" is the concentration of the selected PTE, $PEC_i$ is the probable effect concentration of the selected PTE, and $n$ is the number of studied PTEs. PECQ is classified as follows: PECQ < 0.1, nontoxic; 0.1 < PECQ < 1.5, slightly toxic; 1.5 < PECQ < 2.3, moderately toxic; PECQ > 2.3, heavily toxic.

#### 2.3.5 Statistical analysis and mapping

Descriptive statistics of PTEs such as minimum value, maximum value, mean value, median, and standard deviation (SD), were obtained by SPSS 21.0 (IBM, USA). Kruskal–Wallis test was analyzed by SPSS 21.0 (IBM, USA) to compare the significant difference of PTM concentrations in different drainages and sampling periods considering the data do not have a normal distribution. Origin 2019 (Origin Lab Corporation, USA) software was used for correlation and hierarchical clustering analysis. ArcMap™ 10.2 (ESRI Inc., USA) was used for spatial analysis to examine the spatial distribution pattern and variability of PTE contamination levels and ecological risk.

**Table 3** Descriptive statistics for PTEs (mg kg$^{-1}$) in stream sediments in this study and in the 1980s from the Hetaoping and Heiyanao drainages and in Yunnan Province and sediment quality guidelines (SQGs)

| | | As | Cd | Cr | Cu | Hg | Ni | Pb | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|
| Total samples in this study | *N* | 35 | 35 | 35 | 35 | 35 | 35 | 35 | 35 | 35 |
| | Mean | 156 | 4.62 | 94 | 224 | 0.40 | 39 | 593 | 1382 | 145 |
| | Median | 112 | 4.77 | 91 | 193 | 0.20 | 38 | 498 | 1104 | 146 |
| | SD | 116.93 | 3.32 | 28 | 218 | 0.54 | 10 | 483 | 1241 | 42 |
| | Min | 14 | 0.15 | 46 | 39 | 0.06 | 11 | 31 | 99 | 54 |
| | Max | 628 | 11.84 | 171 | 1337 | 2.88 | 64 | 2145 | 4969 | 261 |
| Samples in this study, Hetaoping drainage | *N* | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 |
| | Mean | 175 | 3.22 | 104 | 214 | 0.28 | 42 | 370 | 726 | 145 |
| | Median | 171 | 2.64 | 100 | 182 | 0.14 | 40 | 288 | 620 | 133 |
| | SD | 133.78 | 2.47 | 27.62 | 251.55 | 0.37 | 10.60 | 247.96 | 476.25 | 48.93 |
| | Min | 14 | 0.15 | 46 | 39 | 0.06 | 11 | 31 | 99 | 54 |
| | Max | 628 | 8.10 | 171 | 1337 | 1.48 | 64 | 1058 | 1628 | 261 |
| Samples in this study, Heiyanao drainage | *N* | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| | Mean | 109 | 8.14 | 71 | 249 | 0.69 | 31 | 1152 | 3022 | 146 |
| | Median | 104 | 7.57 | 72 | 226 | 0.47 | 31 | 1147 | 2831 | 149 |
| | SD | 22.48 | 2.50 | 6.83 | 96.82 | 0.77 | 3.56 | 481.72 | 1016.10 | 18.23 |
| | Min | 77 | 5.34 | 59 | 135 | 0.36 | 26 | 645 | 1825 | 105 |
| | Max | 142 | 11.84 | 84 | 428 | 2.88 | 38 | 2145 | 4969 | 170 |
| Samples in the 1980s for these two drainages | *N* | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 | 12 |
| | Mean | 97 | 1.12 | 96 | 68 | 0.07 | 51 | 195 | 445 | 210 |
| | Median | 68 | 0.72 | 93 | 65 | 0.06 | 48 | 131 | 228 | 214 |
| | SD | 95.68 | 1.13 | 28.62 | 41.47 | 0.04 | 11.95 | 181.26 | 455.72 | 40.24 |
| | Min | 16 | 0.19 | 66 | 27 | 0.04 | 39 | 28 | 77 | 133 |
| | Max | 365 | 3.90 | 173 | 181 | 0.16 | 82 | 523 | 146 | 257 |
| Samples in the 1980s, Hetaoping drainage | *N* | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| | Mean | 105 | 1.01 | 90 | 69 | 0.07 | 49 | 186 | 453 | 203 |
| | Median | 79 | 0.33 | 93 | 58 | 0.06 | 48 | 92 | 191 | 202 |
| | SD | 103.84 | 1.21 | 16.61 | 45.84 | 0.04 | 7.69 | 197.49 | 496.40 | 40.29 |
| | Min | 16 | 0.19 | 66 | 27 | 0.04 | 39 | 28 | 77 | 133 |
| | Max | 365 | 3.90 | 116 | 181 | 0.16 | 68 | 523 | 1460 | 257 |

**Table 3** (continued)

| | | As | Cd | Cr | Cu | Hg | Ni | Pb | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|
| Samples in the 1980s, Heiyanao drainage | *N* | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| | Mean | 59 | 1.65 | 128 | 67 | 0.08 | 64 | 238 | 406 | 246 |
| | Median | 59 | 1.65 | 128 | 67 | 0.08 | 64 | 238 | 406 | 246 |
| | SD | 11.60 | 0.42 | 64.42 | 0.49 | 0.06 | 25.60 | 77.07 | 251.02 | 12.02 |
| | Min | 51 | 1.35 | 82 | 66 | 0.04 | 46 | 183 | 228 | 237 |
| | Max | 67 | 1.95 | 173 | 67 | 0.13 | 82 | 292 | 583 | 254 |
| Samples in the 1980s, Yunnan Province | *N* | 101,557 | 101,557 | 101,557 | 101,557 | 101,557 | 101,557 | 101,557 | 101,557 | 101,557 |
| | Mean | 21 | 0.41 | 101 | 50 | 1.14 | 45 | 46 | 100 | 319 |
| | Median | 10 | 0.15 | 72 | 29 | 0.04 | 33 | 26 | 76 | 286 |
| | SD | 142.54 | 5464.37 | 119.88 | 82.13 | 21,231.71 | 55.15 | 359.09 | 389.46 | 171.69 |
| | Min | 0.05 | 0.00 | 0.20 | 0.50 | 0.00 | 0.10 | 0.20 | 0.10 | 0.50 |
| | Max | 36,053 | 759 | 9340 | 6046 | 2190 | 4580 | 39,300 | 45,360 | 19,576 |
| SQGs | TEC | 9.79 | 0.99 | 43.4 | 31.6 | 0.18 | 22.7 | 35.8 | 121 | |
| | PEC | 33 | 4.98 | 111 | 149 | 1.06 | 48.6 | 128 | 459 | |

*SQGs* sediment quality guidelines (MacDonald et al. 2000), *TEC* threshold effect concentration, *PEC* probable effect concentration

## 3 Results and discussion

### 3.1 Concentration and spatial distribution of PTEs in stream sediments

The descriptive statistics of the analyzed PTEs from the collected stream sediments in the drainages of the Hetaoping and Heiyanao deposits in this study and stream sediments collected in the RGNR in the 1980s, as well as the SQG values (MacDonald et al. 2000), are listed in Table 3. The Kruskal–Wallis test results are shown in Table 4.

With the exception of Cr and Ni, all the studied PTEs are obviously above their regional background values. The median values of As, Cd, Cu, Hg, Pb, and Zn in the two drainages are 12, 32, 7, 5, 19, and 15 times greater than the values in the stream sediments of Yunnan Province, respectively. In the Hetaoping drainage, the values are 18, 18, 6, 3, 11, and 8, while in the Heiyanao drainage, the values are 11, 50, 8, 12, 44, and 37. As shown in Tables 3 and 4, the concentrations of Cd, Hg, Pb, and Zn in the Heiyanao drainage are significantly higher than those in the Hetaoping drainage.

The spatial distributions of PTEs in stream sediments along the two drainages are shown in Fig. 2. Arsenic, Cd, Cu, Hg, Pb, and Zn have comparable spatial distributions. In the Hetaoping drainage, the concentrations of As, Cd,

**Table 4** Kruskal–Wallis test to compare the significant difference of PTM concentrations in different drainages and sampling periods

| Hypothesis | PTMs | *P* | Result |
|---|---|---|---|
| PTM concentrations no significant difference between Hetaoping and Heiyanao drainage | As | 0.401 | Ture |
| | Cd | < 0.001 | False |
| | Cr | < 0.001 | False |
| | Cu | 0.080 | True |
| | Hg | < 0.001 | False |
| | Ni | < 0.001 | False |
| | Pb | < 0.001 | False |
| | Zn | < 0.001 | False |
| PTM concentrations no significant difference sampled in 1980s and 2017 in these two drainages | As | 0.034 | False |
| | Cd | < 0.001 | False |
| | Cr | 0.884 | True |
| | Cu | < 0.001 | False |
| | Hg | < 0.001 | False |
| | Ni | < 0.001 | False |
| | Pb | 0.002 | False |
| | Zn | 0.003 | False |

$p > 0.05$ means the hypotheses is true, PTMs concentrations no significant difference between Hetaoping and Heiyanao drainage or no significant difference sampled in 1980s and 2017 in these two drainages; $p < 0.05$ means the hypotheses is false, PTMs concentrations has significant difference between Hetaoping and Heiyanao drainage or has significant difference sampled in 1980s and 2017 in these two drainages

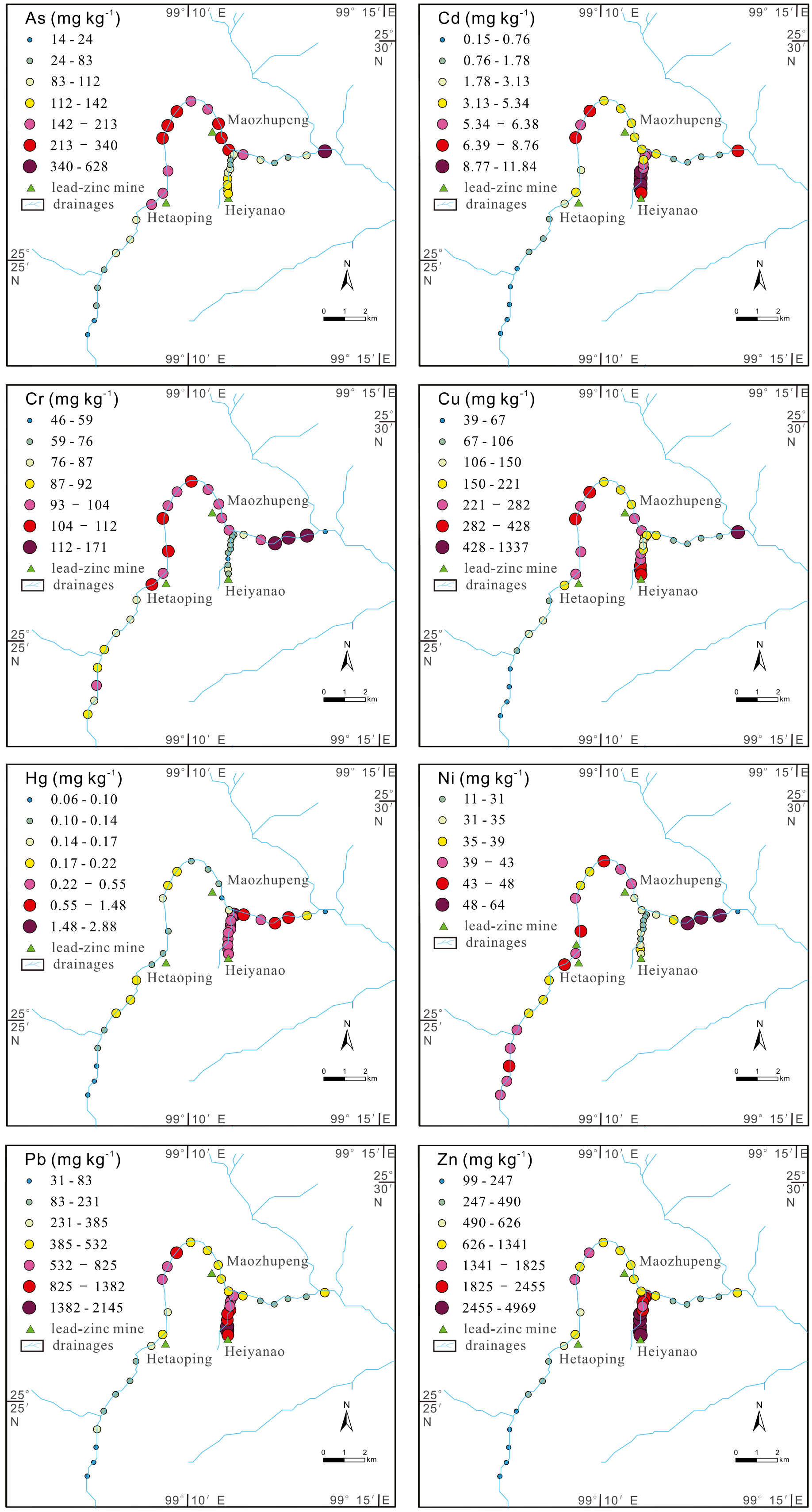


**Fig. 2** The spatial distribution of PTEs in stream sediments along the Hetaoping and Heiyanao drainages

Cu, Hg, Pb, and Zn increase gradually toward the Hetaoping and Maozhupeng deposits and decrease gradually away from the mines. The maximum concentrations of these metals are not in the same location as the deposits but downstream at various distances. This indicates that these metals migrate with water flow and are deposited downstream of the mining area (Goldhaber et al. 2009). Among these elements, Hg migrates farthest. On the other hand, Cr and Ni show similar spatial distributions. The higher concentrations in the upper and lower reaches may be affected by the mafic rock parent materials.

## 3.2 PTE contamination assessment

### 3.2.1 Evaluation by assessment indicators

For this study, we use the PTE median values of the stream sediments of Yunnan Province collected during the RGNR program of the 1980s as a background. Descriptive statistics of $I_{geo}$ values are shown in Table 5. The spatial distributions of $I_{geo}$ of the studied PTEs are shown in Fig. 3.

Chromium and Ni show uncontaminated levels for most samples by the evaluated $I_{geo}$ (Table 5 and Fig. 3).

**Table 5** Descriptive statistics for PTE contamination levels and ecological risks evaluated by indictors

| | | As | Cd | Cr | Cu | Hg | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| $I_{geo}$ | *N* | 35 | 35 | 35 | 35 | 35 | 35 | 35 | 35 |
| | Mean | 3.10 | 3.74 | −0.24 | 1.97 | 1.99 | −0.42 | 3.40 | 2.96 |
| | Median | 2.98 | 4.41 | −0.23 | 2.14 | 1.71 | −0.39 | 3.67 | 3.28 |
| | SD | 1.06 | 1.66 | 0.40 | 1.03 | 1.33 | 0.44 | 1.40 | 1.51 |
| | Min | −0.04 | −0.55 | −1.22 | −0.18 | 0.05 | −2.25 | −0.35 | −0.19 |
| | Max | 5.46 | 5.72 | 0.67 | 4.93 | 5.55 | 0.37 | 5.78 | 5.45 |
| $E_r^i$ | *N* | 35 | 35 | 35 | 35 | 35 | 35 | 35 | 35 |
| | Mean | 164.11 | 924.88 | 2.64 | 38.37 | 388.34 | 5.84 | 114.09 | 18.28 |
| | Median | 118.15 | 954.44 | 2.55 | 33.10 | 196.93 | 5.74 | 95.69 | 14.60 |
| | SD | 123.08 | 664.57 | 0.78 | 37.28 | 524.89 | 1.55 | 92.89 | 16.42 |
| | Min | 14.61 | 30.82 | 1.29 | 6.63 | 62.12 | 1.58 | 5.87 | 1.31 |
| | Max | 660.97 | 2368.98 | 4.78 | 228.88 | 2808.98 | 9.71 | 412.50 | 65.73 |
| PERI | *N* | 35 | | | | | | | |
| | Mean | 1656.54 | | | | | | | |
| | Median | 1555.62 | | | | | | | |
| | SD | 1029.64 | | | | | | | |
| | Min | 141.04 | | | | | | | |
| | Max | 4378.78 | | | | | | | |
| SQGs | < TEC | 0 (0.00%) | 5 (14.29%) | 0 (0.00%) | 0 (0.00%) | 15 (42.85%) | 1 (2.86%) | 1 (2.86%) | 2 (5.71%) |
| | TEC-PEC | 2 (5.71%) | 10 (28.57%) | 31 (88.57%) | 13 (37.14%) | 18 (51.43%) | 31(88.57%) | 2 (0.00%) | 8 (22.86%) |
| | > PEC | 33 (94.29%) | 15 (42.86%) | 4 (11.43%) | 22 (62.86%) | 3 (8.57%) | 3 (8.57%) | 32 (91.43%) | 25 (71.43%) |
| PECQ | *N* | 35 | | | | | | | |
| | Mean | 2.10 | | | | | | | |
| | Median | 2.05 | | | | | | | |
| | SD | 1.15 | | | | | | | |
| | Min | 0.39 | | | | | | | |
| | Max | 4.88 | | | | | | | |
| EF | *N* | 35 | 35 | 35 | 35 | 35 | 35 | 35 | 35 |
| | Mean | 3.23 | 6.76 | 1.49 | 6.69 | 7.36 | 1.14 | 4.93 | 5.73 |
| | Median | 2.87 | 6.05 | 1.37 | 4.91 | 4.65 | 1.06 | 4.45 | 4.00 |
| | SD | 3.76 | 6.11 | 0.54 | 11.97 | 9.37 | 0.36 | 4.07 | 5.85 |
| | Min | 0.20 | 0.19 | 0.80 | 0.71 | 1.12 | 0.59 | 0.21 | 0.28 |
| | Max | 22.38 | 30.04 | 2.66 | 73.10 | 54.53 | 1.94 | 15.49 | 21.18 |

$I_{geo}$ geo-accumulation index, calculated using PTE median values of the stream sediments from Yunnan Province collected in the 1980s as background values. $E_r^i$ and *PERI* potential ecological risk index for individual PTE and total studied PTEs, calculated using PTE median values of the stream sediments of Yunnan Province collected in the 1980s as background values. *SQGs* sediment quality guidelines (MacDonald et al. 2000), *TEC* threshold effect concentration, *PEC* probable effect concentration, *EF* enrichment factor, calculated using Zr as the reference element and the average (mean) concentrations of PTEs in separate stream drainages from the 1980s as background values

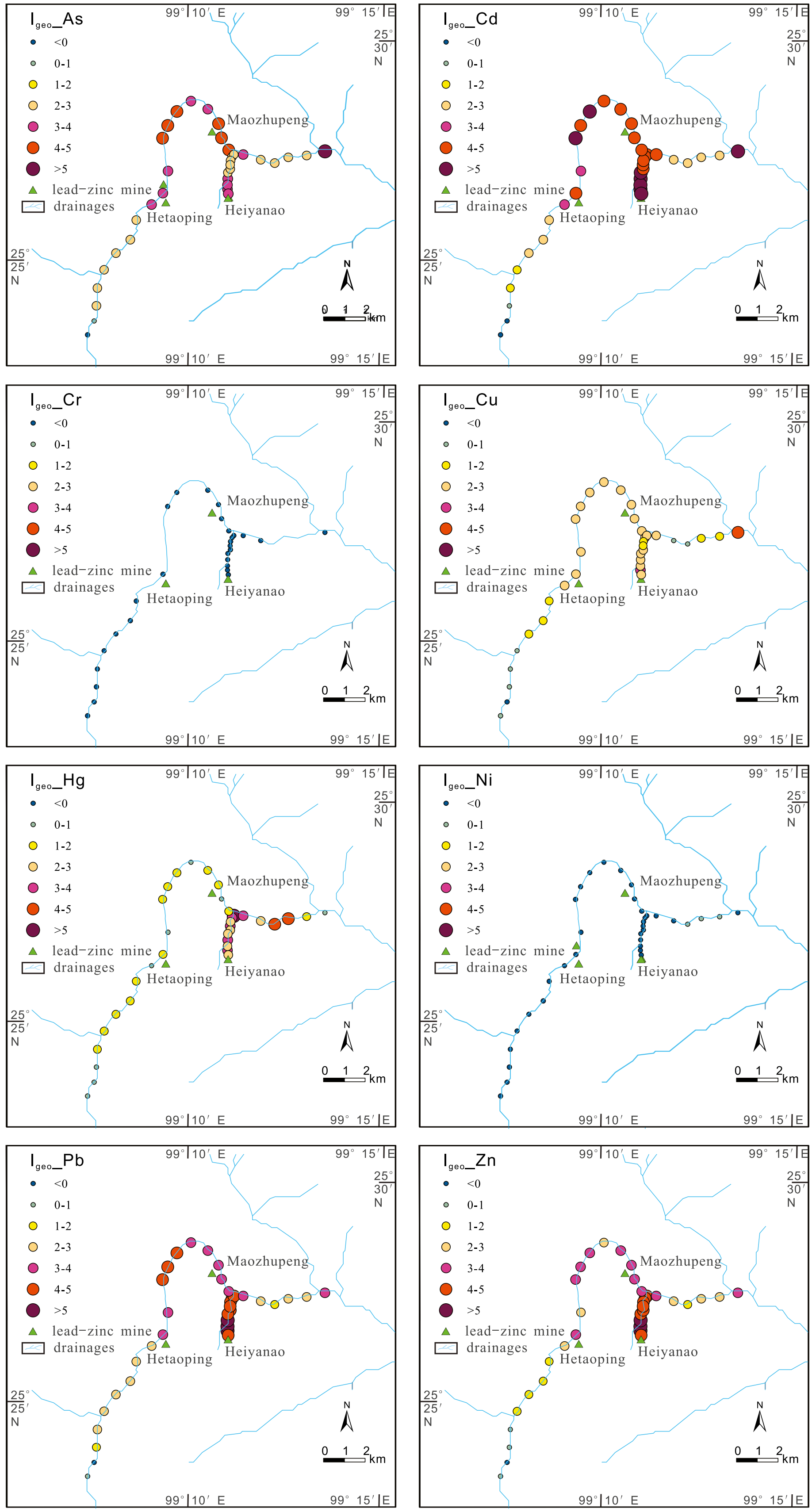


**Fig. 3** The spatial distribution of PTE contamination levels evaluated by geo-accumulation index ($I_{geo}$) in stream sediments along the Hetaoping and Heiyanao drainages

However, As, Cd, Cu, Pb, and Zn showed moderately to highly contaminated levels to extremely contaminated levels near the Hetaoping and Maozhupeng deposits; moderately contaminated levels to uncontaminated levels away from the mine in the Hetaoping drainage; and these elements display moderately contaminated levels to extremely contaminated levels in the Heiyanao drainage. Hg shows moderately contaminated levels to highly to extremely contaminated levels in the Hetaoping drainage and moderately to highly contaminated levels to extremely contaminated levels in the Heiyanao drainage. Similar to the distribution with single metals, the highest contaminated levels are not in the same location as the mine but the downstream reaches at variable distances.

### 3.2.2 Potential ecological risk associated with PTEs

To assess the potential impact of a given PTE and all the studied PTEs in stream sediments on ecosystems, the potential ecological risk ($E_r^i$ and PERI) are used in this study. The descriptive statistics and the spatial distribution of $E_r^i$ and PERI of the studied PTEs are shown in Table 5 and Fig. 4, respectively. In the same way, we use the stream sediments

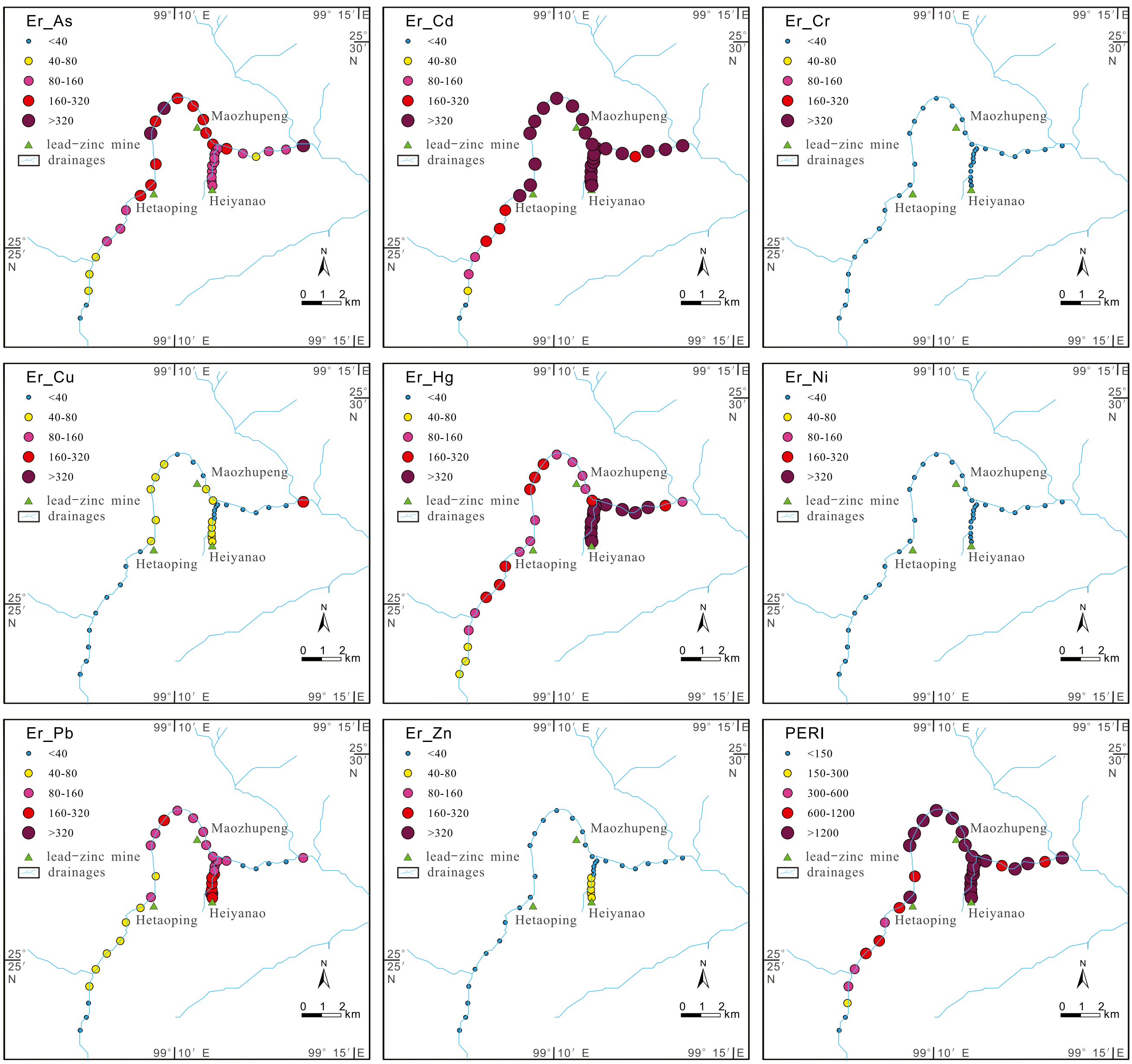


**Fig. 4** The spatial distribution of PTE ecological risks evaluated by potential ecological risk indices ($E_r^i$ and PERI) in stream sediments along the Hetaoping and Heiyanao drainages

of Yunnan Province collected in the RGNR program of the 1980s as background.

Chromium, Ni, Zn, and Cu demonstrate a risk degree of "low potential ecological risk," As and Pb show "considerable potential ecological risk," and Cd and Hg demonstrate "very high potential ecological risk," according to the average (mean) and median values $E_r^i$ obtained at all sampling sites (Table 5). The environmental ecological risks of all studied PTEs are ranked as follows: Cd > Hg > As > Pb > Cu > Zn > Ni ≈ Cr. The distributions of As, Cd, Hg, and Pb with $E_r^i$ values > 80 are mainly in the Heiyanao drainage and samples near the Hetaoping and Maozhupeng lead–zinc mines. Cadmium and Hg posed higher ecological risks than the other PTEs due to their higher toxic response factors (Hakanson 1980). Zinc and Cu do not show risk levels higher than "moderate risk" due to their low toxic response factors, even though their concentrations are higher in sediments. Comparing the ecological risks in these two drainages, the Heiyanao drainage shows much more than the Heiyanao drainage, especially for As, Cd, Hg, Pb, and Zn. Except for three samples in the upper reaches of the Hetaoping drainage, all samples in the Hetaoping and Heiyanao drainages show considerable potential ecological risk according to the PERI results (Fig. 4).

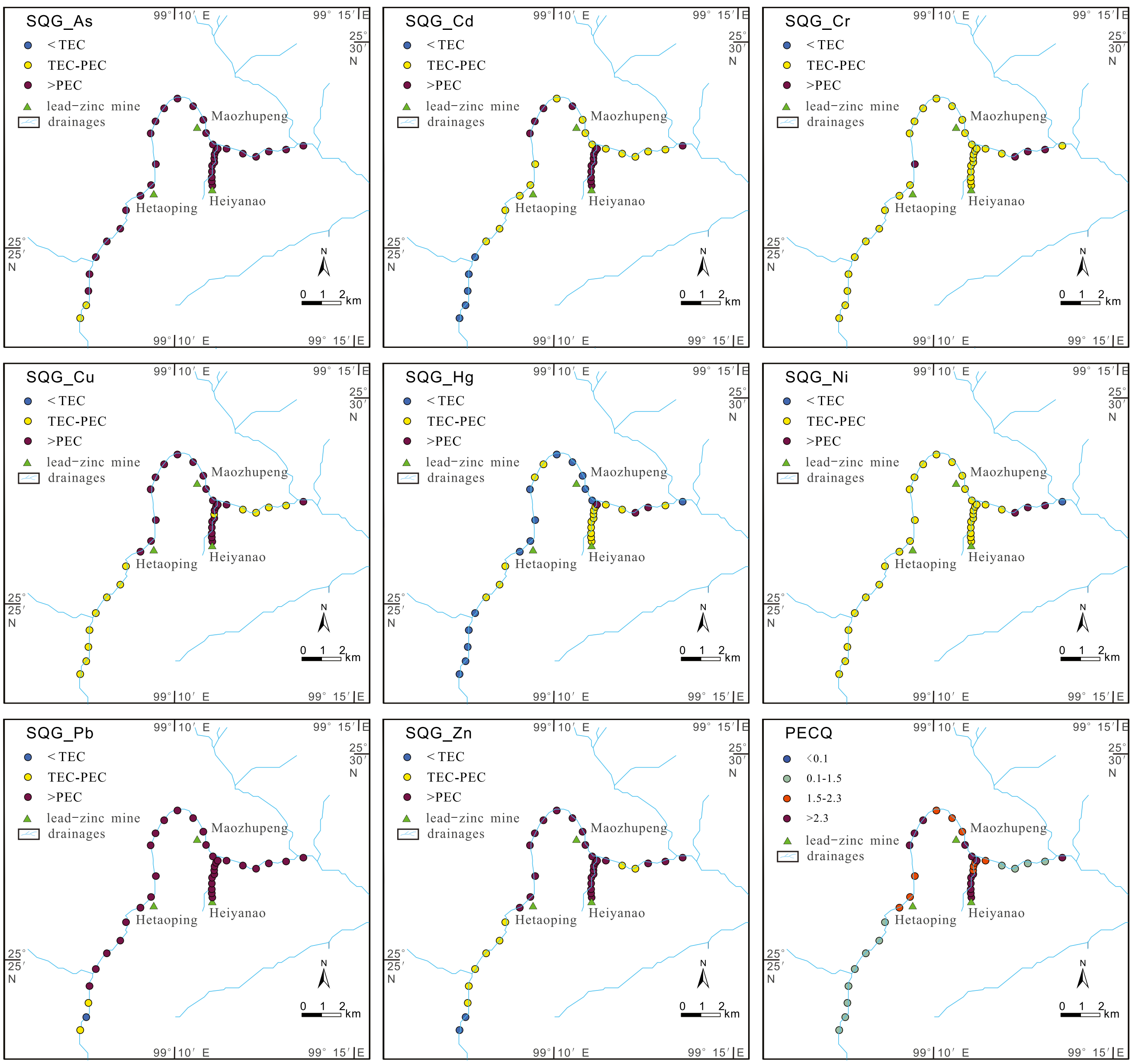


**Fig. 5** The spatial distribution of PTE ecological risks evaluated by sediment quality guidelines (SQGs) and mean probable effect concentration quotient (PECQ) in stream sediments along the Hetaoping and Heiyanao drainages

**Table 6** The Pearson correlation coefficients of the PTEs in this study

| | As | Cd | Cr | Cu | Hg | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|
| As | 1 | | | | | | | |
| Cd | 0.413* | 1 | | | | | | |
| Cr | −0.162 | −0.462** | 1 | | | | | |
| Cu | 0.852** | 0.557** | −0.370* | 1 | | | | |
| Hg | −0.224 | 0.133 | 0.124 | −0.106 | 1 | | | |
| Ni | −0.405* | −0.540** | 0.941** | −0.562** | 0.08 | 1 | | |
| Pb | 0.159 | 0.920** | −0.425* | 0.345* | 0.1 | −0.424* | 1 | |
| Zn | 0.063 | 0.921** | −0.461** | 0.309 | 0.222 | −0.451** | 0.961** | 1 |

*Correlation is significant at the $p<0.05$ level (single tailed); **correlation is significant at the $p<0.01$ level (single tailed)

When comparing the results to the SQGs (Table 5 and Fig. 5), except for 42.8% (15 samples) of Hg, 2.86% (1 sample) of Ni, 2.86% (1 sample) of Pb, and 5.71% (2 samples) of Zn, the PTE concentrations are higher than the TEC, indicating that the occurrence of biological effects is possible. In particular, 94.29% (33 samples) of As, 42.86% (15 samples) of Cd, 11.43% (4 samples) of Cr, 62.86% (22 samples) of Cu, 8.57% (3 samples) of Hg, 8.57% (3 samples) of Ni, 91.43% (32 samples) of Pb, and 71.43% (25 samples) of Zn are higher than PEC, indicating probable effects where adverse biological outcomes frequently occur. The samples with Cd, Cu, and Hg exceeding PEC are mainly in the Heiyanao drainage and samples near the Hetaoping and Maozhuping deposits, while for As and Pb, the samples are mostly distributed throughout the drainage system. These results differ from the calculated results of $E_r^i$, especially the SQG results, which yield high risks for Cr and Ni. Since the $E_r^i$ values associated with sediment metals are more dominated by the concentration of bioavailable forms, the SQGs are based on the total metal concentrations (MacDonald et al. 2000; Birch and Apostolatos 2013; Xu et al. 2020). According to the PECQ results (Table 5 and Fig. 5), samples from the Heiyanao drainage and samples near the Hetaoping and Maozhuping deposits have moderately to heavily toxic risk, and the remaining samples are at slightly toxic levels.

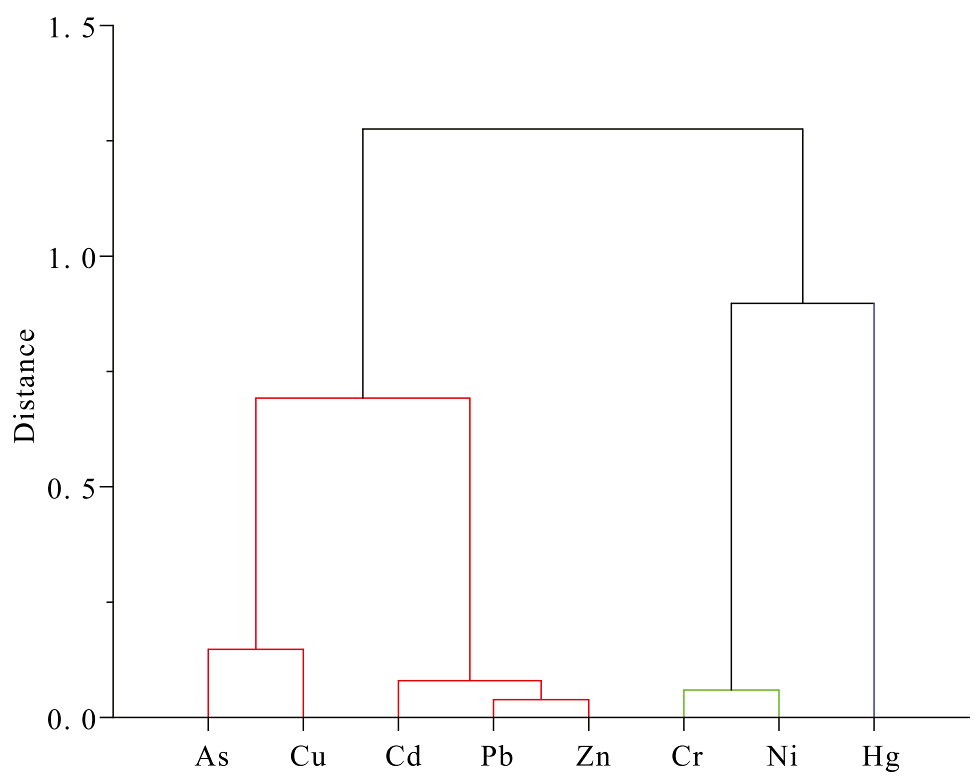


**Fig. 6** The hierarchical clustering analysis of PTEs based on Pearson correlation coefficients

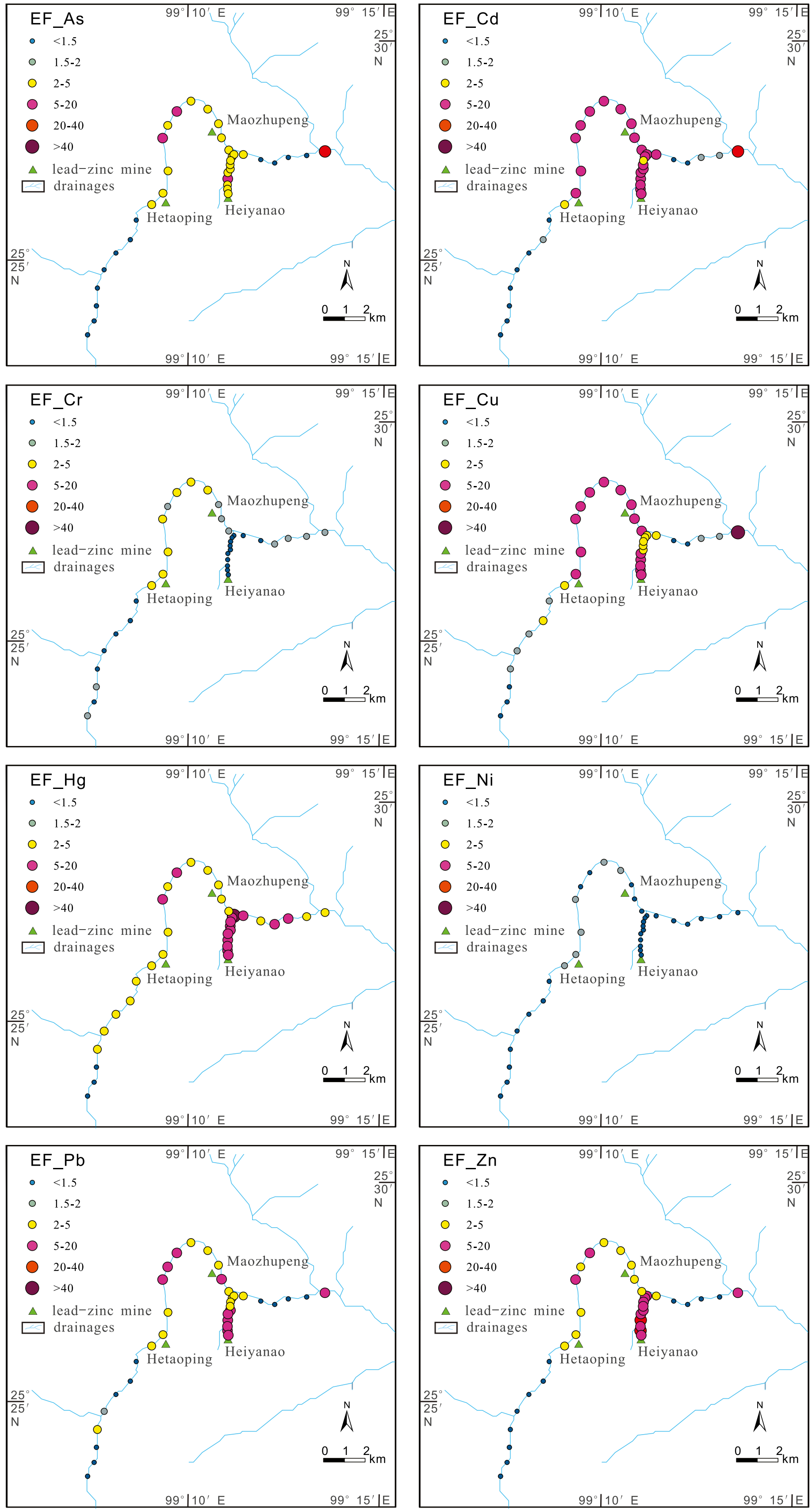


**Fig. 7** The spatial distribution of PTE contamination/source identification evaluated by the enrichment factor (EF) in stream sediments along the Hetaoping and Heiyanao drainages

### 3.3 Potential source identification

In the same river systems, correlation analysis can reveal the source relationships of different PTEs. A correlation between metals indicates that they may have similar sources; no correlation implies that they are from different sources (Zhang et al. 2010; Suresh et al. 2011; Ke et al. 2017; Xu et al. 2020). Table 6 shows the Pearson correlation analysis results. The concentration of Cd is significantly positively correlated with Cu, Pb, and Zn at the $p < 0.01$ level, and positively correlated with As at the $p < 0.05$ level. Positive correlations at the $p < 0.01$ level are found between Cr and Ni. In contrast, no significant correlation between Hg and other metals is found. The results indicate that As, Cd, Cu, Pb, and Zn may come from the same source, Cr and Ni may come from another source, and Hg may come from other separate sources. Figure 6 shows the hierarchical clustering based on Pearson correlation coefficients, which indicate the same results as the correlation analysis: As, Cd, Cu, Pb, and Zn from one source, Cr and Ni from another source, and Hg from a third source.

The enrichment factor (EF) is widely used to distinguish PTEs from natural or anthropogenic sources (Li et al. 2012; Dou et al. 2013; Chen et al. 2019). Reimann and Caritat (2000, 2005) critically assessed and warned against the shortcomings of EF because different background values may yield different results. In this study, we carefully compare the calculation results based on different background values and finally use the average (mean) concentrations of PTEs in separate stream drainages from the 1980s as background values to represent the natural baselines before large-scale mining. Descriptive statistics of EF values are shown in Table 5. The spatial distributions of the EFs of the studied PTEs are shown in Fig. 7.

According to the statistical analysis and EF spatial distribution results, we suggest three main sources of these PTEs. (1) Cr and Ni are from natural sources because their EF values are < 1.5 or close to 1.5, which reflects a natural source, and are mainly contributed by the natural weathering of parent materials; (2) As, Cd, Cu, Pb, and Zn in the Heiyanao drainage and near the Hetaoping and Maozhupeng mines in the Hetaoping drainage are from anthropogenic sources, mainly contributed by lead–zinc mining activities. Conversely, for locations away from the mining center, these elements are also derived from natural sources; (3) Hg also originates from anthropogenic sources, but its sources are different from those of As, Cd, Cu, Pb, and Zn.

**Table 7** The temporal accumulation of PTEs (mg $kg^{-1}$) in stream sediments calculated based on average (mean) and median values

| | | This study | | | 1980s | | | Ratio | |
|---|---|---|---|---|---|---|---|---|---|
| | | *N* | Mean[a] | Median[b] | N | Mean[c] | Median[d] | $(a-c)/c*100$ | $(b-d)/d*100$ |
| Two drainages | As | 35 | 156 | 112 | 1 | 97 | 68 | 60 | 65 |
| | Cd | 35 | 4.62 | 4.77 | 12 | 1.12 | 0.72 | 314 | 563 |
| | Cr | 35 | 94 | 91 | 12 | 96 | 93 | −2 | −2 |
| | Cu | 35 | 224 | 19 | 12 | 68 | 65 | 229 | 198 |
| | Hg | 35 | 0.40 | 0.20 | 12 | 0.07 | 0.06 | 433 | 220 |
| | Ni | 35 | 39 | 38 | 12 | 51 | 48 | −24 | −20 |
| | Pb | 35 | 593 | 498 | 12 | 195 | 131 | 205 | 281 |
| | Zn | 35 | 1382 | 1104 | 12 | 445 | 228 | 210 | 385 |
| Hetaoping drainage | As | 25 | 175 | 171 | 10 | 105 | 79 | 66 | 118 |
| | Cd | 25 | 3.22 | 2.64 | 10 | 1.01 | 0.33 | 219 | 713 |
| | Cr | 25 | 104 | 100 | 10 | 90 | 93 | 15 | 7 |
| | Cu | 25 | 214 | 182 | 10 | 69 | 58 | 213 | 214 |
| | Hg | 25 | 0.28 | 0.14 | 10 | 0 | 0 | 285 | 128 |
| | Ni | 25 | 42 | 40 | 10 | 49 | 48 | −14 | −16 |
| | Pb | 25 | 370 | 288 | 10 | 186 | 92 | 99 | 212 |
| | Zn | 25 | 726 | 620 | 10 | 453 | 191 | 60 | 226 |
| Heiyanao drainage | As | 10 | 109 | 104 | 2 | 59 | 59 | 85 | 77 |
| | Cd | 10 | 71 | 72 | 2 | 1.65 | 1.65 | 4209 | 4251 |
| | Cr | 10 | 71 | 72 | 2 | 128 | 128 | −44 | −44 |
| | Cu | 10 | 249 | 226 | 2 | 67 | 67 | 274 | 240 |
| | Hg | 10 | 0.69 | 0.47 | 2 | 0.08 | 0.08 | 721 | 461 |
| | Ni | 10 | 31 | 31 | 2 | 64 | 64 | −51 | −52 |
| | Pb | 10 | 1152 | 1147 | 2 | 238 | 238 | 385 | 383 |
| | Zn | 10 | 3022 | 2831 | 2 | 406 | 406 | 645 | 598 |

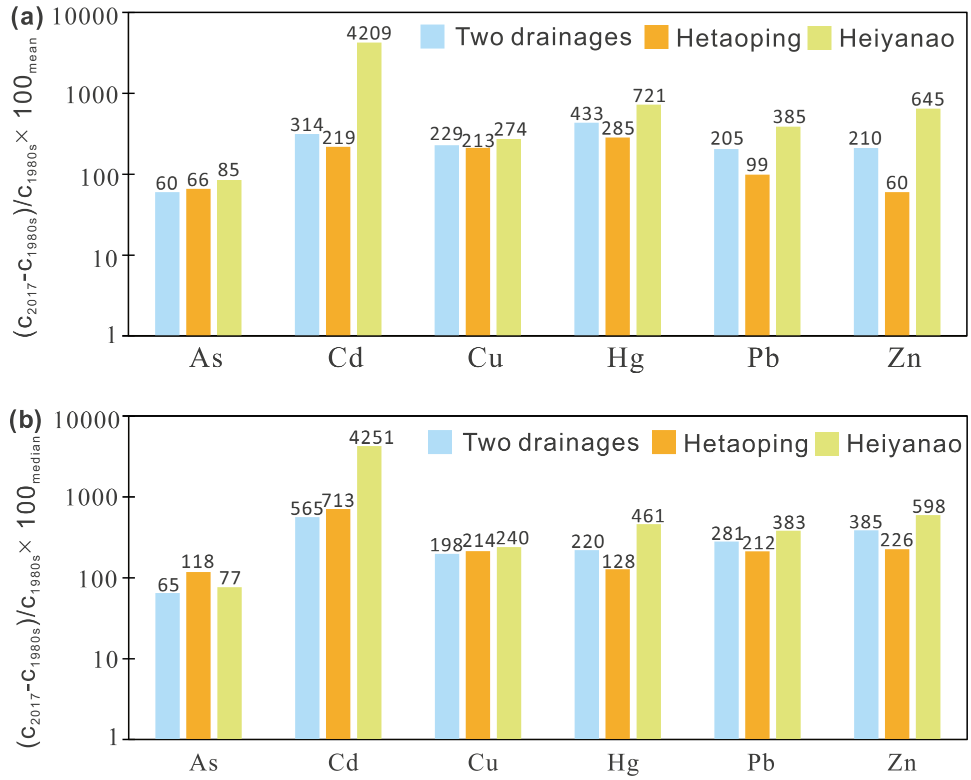


**Fig. 8** The bar charts of PTE accumulation in stream drainages

### 3.4 Temporal accumulation analysis

To analyze the temporal accumulation of the studied PTEs in these mine drainages, we compare our dataset with datasets from the 1980s, which indicate the PTE status prior to large-scale mining activities.

The temporal accumulation of PTEs in stream sediments calculated based on average (mean) and median values of PTEs in these two periods in the Hetaoping drainage, the Heiyanao drainage, and the two drainages are listed in Table 7. The rates of change are calculated by the mean and median values (Table 7). Compared with those measured in the 1980s (Table 7), the concentrations of As, Cd, Cu, Hg, Pb, and Zn are significantly increased in stream sediment samples collected in 2017. The results reflect the influence of mining activities in the past 40 years on the accumulation of PTEs in the surrounding stream sediments. Cd is the most metal that has increased the most; it increased 314 (by mean) and 563% (by median) in all samples, 219 (by mean) and 713% (by median) in the Hetaoping drainage, and 4209 (by mean) and 4251% (by median) in the Heiyanao drainage. In contrast, Ni has significantly decreased. To reflect the average increases of metals of each water drainage visually and intuitively, bar charts based on the mean and median are presented (Fig. 8). The metals normally related to lead–zinc mining activities have increased significantly in the Heiyanao drainage than in the Hetaoping drainage; these increases are 60–285% in the Hetaoping drainage sediments and 85–4251% in the Heiyanao drainage sediments. These results indicate PTE dilution by the river in stream sediments due to the wider waterline and greater flow in the Hetaoping drainage and the greater influence of mining activities on the surface environment of the Heiyanao mine than of the Hetaoping mine.

## 4 Conclusions

The following conclusions can be drawn from the above research:

(1) As, Cu, Hg, Pb, and Zn are obviously higher than their regional background values. The concentrations of Cd, Hg, Pb, and Zn in the Heiyanao drainage are significantly higher than in the Hetaoping drainage.
(2) As, Cd, Cu, Hg, Pb, and Zn are found at moderately contaminated to extremely contaminated levels near the Hetaoping and Maozhupeng deposits, as well as in the Heiyanao drainage.
(3) The ecological risks of PTEs are predominantly near the mining center, and the risks rank as follows: Cd > Hg > As > Pb > Cu > Zn > Ni ≈ Cr.
(4) Cr and Ni are from natural sources; As, Cd, Cu, Pb, and Zn come from mining activities near the mining center, as well as natural sources outside the mining

center; Hg originates from other uncertain anthropogenic sources.

(5) Mining activities in the past 40 years have significantly increased As, Cd, Cu, Hg, Pb, and Zn concentrations in the sediments of surrounding streams.

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**Author contribution** All authors contributed to the study conception and design. Li Zhang: conceptualization, formal Analysis, investigation, methodology, software, and writing—original draft. Zheng Yang: software. Qiaolin Wang: software. Fei Guo: software. Min Peng: project administration. Yuntao Song: investigation. Wei Han: investigation. Fei Liu: project administration. Kuo Li: methodology. Hangxin Cheng: project administration and conceptualization.

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**Data availability** Data will be made available on reasonable request.

## Declarations

**Ethics approval** Participation of human or animal subjects did not occur in this study.

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

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