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Pollution and health risk assessment of toxic metal(loid)s in soils under different land use in sulphide mineralized areas

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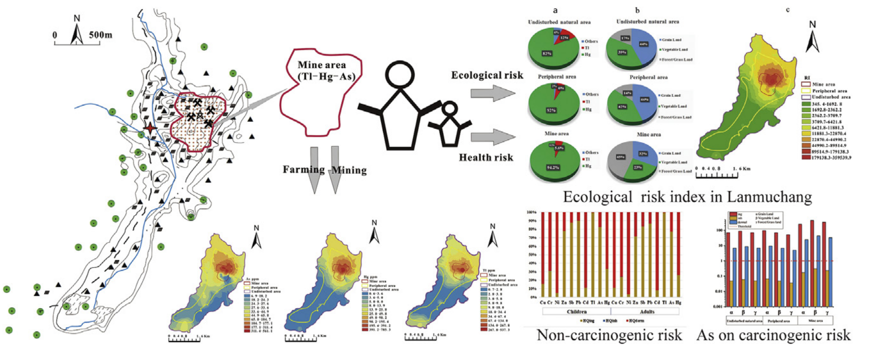
HIGHLIGHTS

- High Tl, Hg and As contents in soils were attributed to natural weathering of sulfide minerals and past sporadic mining.
- Local soils present high ecological risk for Tl and Hg.
- Both children and adults experienced non-carcinogenic potential exposure risk of Tl, Hg and As from local soils.
- Arsenic in soils pose serious carcinogenic exposure risk through ingestion of soil particles.

GRAPHICAL ABSTRACT



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ABSTRACT

Toxic metal(loid) pollution in sulphide mineralized area has been increasingly concerned. In the present study, the pollution characteristics and the health risk of Hg, As, Tl and other metal(loid)s in soils under different land use, from a rural area impacted by Tl-Hg-rich sulphide mineralization, were assessed using statistical analysis, enrichment factor (EF), potential ecological risk index (RI) and health risk assessment model. The results showed that Tl, Hg and As were highly enriched in the mine area due to the historic sporadic mining activities, and Tl, Hg and Sb were enriched in the peripheral area. Hg and Tl pollution in soils of the mine area impacted by past mining activities posed high ecological risk. High contents and enrichment of Tl and Hg in forest/grass land had a greater impact on the ecological risk in the mine area; whereas Tl and Hg in the grain land and vegetable land dominated the soil ecological risk in the peripheral area. Human health risk assessment indicated that children are more sensitive and vulnerable to toxic metal(loid)s in soils than the adults. Hg, Tl and As have potential non-carcinogenic risk to local children and adults. The HQ levels for different exposure pathways of toxic metal(loid)s were in the order of ingestion > dermal contact > air inhalation for Tl and As, and dermal contract > ingestion > air inhalation for Hg. For carcinogenic risk, all the mean CR values of ingestion in the mine area were higher than 10^{-4}, indicating seriously potential risk. The descending order of ILCR via different pathways was the same as the HQ, for which ingestion was predominant, followed by dermal and air inhalation. The findings may help provide basic knowledge and guidelines for toxic metal(loid) pollution remediation in similar sulphide mineralized areas.

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1. Introduction

Soil toxic metal(loid) pollution, threatening the health of both ecosystems and human beings, have attracted increasing environmental concern and become an urgent problem throughout the world (Moreno et al., 1993; Pandey et al., 2003; Feng and Qiu, 2008; Kim et al., 2009; Srinivasa Gowd et al., 2010; Li et al., 2012a; Vaněk et al., 2020). There have over 10 million major contaminated sites worldwide, of which >50% were contaminated with toxic metal(loid)s (Khalid et al., 2017).

Intensive studies for toxic metal(loid) pollution have focused on the concentration distribution, migration and transformation, as well as remediation (Nriagu and Pacyna, 1988; Chen et al., 1997; Sun et al., 2010; Hu and Cheng, 2013; Ha et al., 2014; Li et al., 2014; Vanek et al., 2018). However, soil pollution is generally a combined pollution with multiple metal(loid)s rather than individual metal(loid) (Liu et al., 2017; Zhai et al., 2018; He et al., 2019), and the pollution is originated from either anthropogenic activities such as metal mining/smelting, or geogenic source (Facchinelli et al., 2001). In addition, toxic metal(loid) pollution under different land use may bring different effects (Huang et al., 2018). Therefore, it is critical to have appropriate health risk assessment of soil toxic metal(loid) pollution. Particularly, soils that are derived from sulphide mineralization terrains or partly impacted by past small scale of mining and/or artisanal smelting activities, rather than being disturbed by intensive mining/smelting activities, are required for a full understanding of the geochemical distribution and health risk assessment of toxic metal(loid)s under different land use.

An excellent site that experienced sulphide mineralization of Hg-As-Tl and sporadically artisanal Hg mining/smelting activities (105°30′23″ E, 25°31′28″N) is from Lanmuchang, a rural area in southwestern Guizhou Province, China, where Hg mining/smelting activities were back to the 17th century. This area is located in the geological setting with occurrence of metal(loid) mineralization of Au, Hg, Sb, As and Tl, within a large area of 900,000 km^2 (Xiao et al., 2012). Previous studies have documented that three toxic metal(loid)s of thallium (Tl), mercury (Hg) and arsenic (As) are highly enriched in local soils of Lanmuchang due to sulphide mineralization (lorandite for Tl, cinnabar for Hg, and realgar and orpiment for As, respectively), through both natural processes and human activities (Xiao et al., 2004a), and they are preferentially transferred to locally food crops (Xiao et al., 2004a; Wang et al., 2005; Qiu et al., 2006). However, the absence of detailed knowledge for health risk corresponding to soil toxic metal(loid) pollution, is still a matter of high concern, particularly constrained by different source apportionment and land use. The soil toxic metal(loid)s derived from natural weathering of sulphide minerals and past sporadic sulphide mineral mining/smelting may present different health risks, and a full understanding of such knowledge is beneficial to appropriate approach of pollution remediation. Consequently, the present study aimed to determine the geochemical distribution of soil toxic metal(loid)s under local different land use, and to assess the ecological and health risks of soil toxic metal(loid)s. The findings would be beneficial to similar geo-environmental contexts of soil metal(loid) pollution in many other regions in the world, in terms of various source apportionment and land use.

2. Materials and methods

2.1. Study area

The study area is located at Lanmuchang (105°30′23″E, 25°31′28″N), a small rural area of approximately 1000 inhabitants in southwest Guizhou Province, China. This area presents karst topography, exhibiting a higher elevation in the northwest and a lower elevation in the southeast. The average altitude is 1400 m, and the relative relief is 100–200 m. A detailed description of the local geology was previously reported (Xiao et al., 2003). The Lanmuchang Hg-Tl-As mineralize zone is underlain by Permo-Triassic sedimentary rocks and overlain by Quaternary alluvium. The exposed rocks include limestone, argillite and coal seams. The sulphide mineralization outcrops in the hills, where it is susceptible to weathering and dispersion. The local residents have experienced symptoms associated with chronic Tl poisoning, including weakness, muscle and joint pain, disturbance of vision, hair loss, and high Tl level in urine (Xiao et al., 2007). These symptoms are induced by Tl contaminations in local soils, waters and crops (Xiao et al., 2007), which appears to be due to local sulphide mineralization of Tl, As and Hg, and local sporadic mining activities.

The Lanmuchang area has been widely developed for agricultural and residential purposes, and related disturbances, and for purposes of farming, surface grading and excavations for foundations and septic systems, are very common. The mine-disturbed areas have been treated with ‘fill’ materials variably composed of local soils and mining wastes, whereas the farming and residential areas are largely made up of reworked original surface materials including alluvial and colluvial deposits (Xiao et al., 2004a). The local soils mainly originate from the weathering of outcrops and accumulate naturally on the slightly to moderately steep slope. Through preliminary investigation and previous literature, the local land use type (Fig. 1a) of the past sporadic mine area (MA) mainly refers to forestland and grassland, and local farmers grow vegetables or food crops on some slope soils (Xiao et al., 2004a). Surrounding the mine area, i.e. the peripheral area (PA), is the main residential area and the most intensive cropping area for vegetable land and grain land. The undisturbed natural area (UA) is a bit far away from the mine area and also outside the peripheral area, and the soils are derived from geogenic weathering process. Overall, the local agricultural activities are widely distributed but relatively dispersed. Therefore, in order to obtain comprehensive soil pollution characteristics and provide data support for pollution remediation, it is particularly important to conduct soil survey of different land use in the study area.

2.2. Sampling and analysis

Extensive suites of 217 topsoil samples including 153 from the mine area, 34 from the peripheral area and 30 from the undisturbed natural area, were collected in the study area (Fig. 1b). The soil ssamples were collected using a stainless-steel shovel, and at each site 5 sub-samples (0–20 cm depth) were taken from an area of 2.5 m^2, and mixed into a composite sample, and then kept in polyethylene bags and air-dried in the laboratory pending final processing. Before the experiment, unnecessary materials, such as rhizomes, sands and gravels, were removed from the samples. The soils were passed through a 2-mm sieve for analysis. The sieved fractions were then ground in an agate mortar, and they were further ground to 80-mesh (<180 μm) powder in an agate ball mill.

Approximately 50 mg of the sieved soil samples (<180 μm) for geochemical analysis were digested in a mixture of concentrated acids ($HF/HNO_3/HClO_4$), and the initial contents of Tl, Hg, As and other metal(loid)s were determined using an inductively coupled plasma mass spectrometry (ICP-MS, ELAN DRC-e, Perkin-Elmer, USA). Each soil sample was analyzed with three replicate determinations, and the mean values were obtained.

The detection limit was calculated as average of ten times the standard deviation of the ion counts obtained from the individual procedural reagent blanks (prepared in the same way as the sample decomposition), divided by the sensitivity of standard solution. The detection limit for Tl, Hg, As and other metal(loid)s was 0.01 mg/kg. Standard references of soils GBW07403, GBW07405 and GBW07408 (National Institute of Standard Materials, China) were used to control the analysis quality. The analytical precision was determined by quality assurance/quality control procedures using duplicates, blanks, internal standards (Rh at 500 μg/L) and reference samples, and the result was better than ±10%.

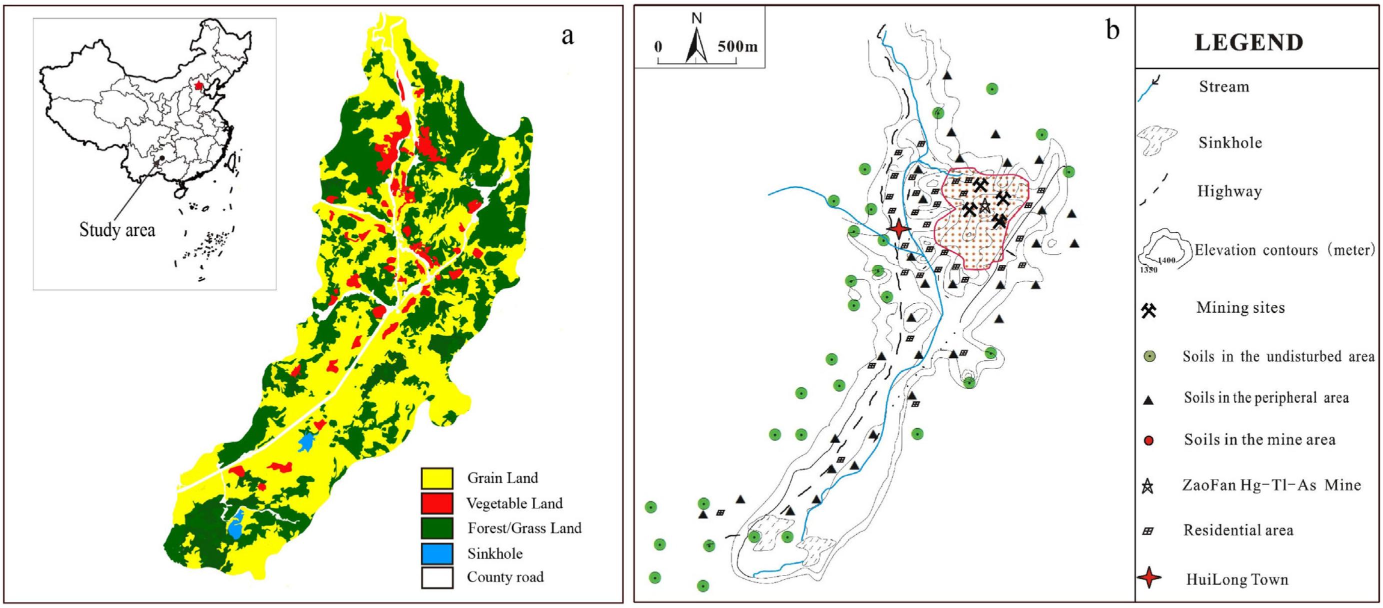

Fig. 1. a. Distribution of land use type in local soils in Lanmuchang area; b. Location of soil sampling sites.

2.3. Assessment of potential ecological risk index and enrichment factor

Potential ecological risk index (RI) represents the sensitivity of the biological community to pollutants and illustrates the resulting potential ecological risk (Hakanson, 1980). The equation used to calculate RI is as follows:

$$RI = \sum\nolimits_{i=1}^{n} E_r^i = \sum\nolimits_{i=1}^{n} T_r^i \times \frac{C_i}{S_i} \tag{1}$$

where n is the number of trace metal(loid), E_r^i represents potential ecological index for a single element. T_r^i is the toxic response factor, and the values for each element increase in the order of Zn(1)<Cr(2)<Pb = Ni = Cu(5)<Sb(7)<As(10)<Cd(30)<Hg = Tl(40), which is shown in Table S1. C_r^i is the actual concentration of the toxic metal(loid) in the soil sample and S_i is the reference value of the toxic metal(loid). The RI results were calculated and classified as low risk (E_r^i<40), moderate risk (40<E_r^i<80), considerable risk (80<E_r^i<160), high risk (160<E_r^i<320), and very high risk (E_r^i>320) (Hakanson, 1980). RI ≤ 150, low ecological risk; 150 ≤ RI ≤ 300, moderate risk; 300 ≤ RI ≤ 600, strong risk; RI ≥ 600, quite strong (Chen et al., 2018).

To assess quantitative levels of anthropogenic input of toxic metal (loid)s into agricultural top soils, the enrichment factor (EF) was calculated and analyzed. EF is standardization of concentration of target element in topsoil sample by the reference element (Tepanosyan et al., 2017). As a reference, local background values were used. A reference element is often a conservative one, such as the most commonly used elements: Ti (Lan et al., 2019), Sc (Hernandez et al., 2003; Kim et al., 2016), Fe (Enamorado-Báez et al., 2015), Mn (Loska et al., 1997), Li (Loring, 1990), Cs (Roussiez et al., 2005; N'guessan et al., 2009), Al (Liu et al., 2019), and Zr (Liu et al., 2013).

In this study, Al, which is considered as an immobile element in the environment, was chosen as the reference element. The enrichment factor was calculated as:

$$EF = (C_i/C_{Ti})/(B_i/B_{Ti}), \tag{2}$$

where C_i is the concentration of the examined element in topsoil sample, C_{Ti} is the concentration of Al in the same sample, B_i and B_{Ti} are background values of the examined element and Al, respectively. EF can assist in differentiating an anthropogenic source from a natural origin (Chen et al., 2014). Value of EF close to 1 indicates that the element has a natural origin, whereas value>10 can be considered to originate mainly from anthropogenic sources (Turner and Simmonds, 2006; Tepanosyan et al., 2017). EF also can be used to assess pollution by toxic metal(loid)s, particularly EF was classified as deficiency to no enrichment (EF ≤ 1), minimal enrichment (1<EF < 2), moderate enrichment (2 < EF < 5), significant enrichment (5 < EF < 20), very high enrichment (20 < EF < 40), and extremely high enrichment (EF>40) (Lu et al., 2009; Tepanosyan et al., 2017).

2.4. Human health risk assessment

The exposure health influence of soil toxic metal(loid)s to the human health is assessed by the US Environmental Protection Agency (EPA) human health evaluation method (US EPA, 2001). There are three major exposure pathways for adults and children to toxic metal (loid)s in soils, i.e. ingestion, inhalation, and dermal contact (Wei and Yang, 2010; Du et al., 2013).

Health risk assessments of toxic metal(loid)s in soils are widely used to quantify both carcinogenic and non-carcinogenic risks to humans via ingestion, inhalation and dermal contact exposure pathways. The average daily exposure doses (ADDs) of toxic metal(loid)s via various exposure pathways can be calculated as follows (USEPA, 1986; USEPA, 1996a; USEPA, 2002; Praveena et al., 2015). In this study, the average daily doses (ADDs) (mg/ kg day^{-1}) of potentially toxic metal(loid)s via ingestion (ADD_{ing}), dermal contact (ADD_{derm}), and inhalation (ADD_{inh}) for both adults and children were calculated by using Eqs. (3)–(5):

$$ADD_{ing} = \frac{C \times IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \tag{3}$$

$$ADD_{inh} = \frac{C \times InhR \times EF \times ED}{PEF \times BW \times AT} \tag{4}$$

$$ADD_{dermal} = \frac{C \times SA \times SL \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \tag{5}$$

where C is the concentration of topsoil toxic metal(loid) (mg/kg), and all the other parameters were showed in Table S2.

For carcinogenic metalloid, arsenic, the lifetime average daily doses (LADDs) were used to the assessment of cancer risk for three exposure routes and calculated as follow Eqs. (6)–(8) (USEPA, 1996a, 1996b; US EPA, 2002; Wang et al., 2016).

$$LADD_{ing} = \frac{C \times EF}{AT} \times \left(\frac{IngR_{child} \times ED_{child}}{BW_{child}} + \frac{IngR_{adult} \times ED_{adult}}{BW_{adult}} \right) \times 10^{-6} \quad (6)$$

$$LADD_{inh} = \frac{C \times EF}{AT \times PEF} \times \left(\frac{InhR_{child} \times ED_{child}}{BW_{child}} + \frac{InhR_{adult} \times ED_{adult}}{BW_{adult}} \right) \quad (7)$$

$$LADD_{dermal} = \frac{C \times EF \times ABS}{AT} \times \left(\frac{SL_{child} \times SA_{child} \times ED_{child}}{BW_{child}} + \frac{SL_{adult} \times SA_{adult} \times ED_{adult}}{BW_{adult}} \right) \times 10^{-6} \quad (8)$$

The non-cancer risk is assessed by the total hazard index (HI), which is the sum of the hazard quotient (HQ) in different exposure pathways. The hazard quotient is determined by the quotient of the daily exposure doses (ADD) and its corresponding reference dose (RfD). The HI and HQ of soil toxic metal(loid)s are calculated as Eq. (9).

$$HI = \sum HQ_i = \sum \frac{ADD_i}{RFD_i} \quad (9)$$

If the values of HI (or HQ) between 1 and 10, it means possible adverse health effects; if HI (or HQ) < 1, it indicates no significant risk of non-carcinogenic effects; if HI (or HQ)>10, it means high chronic risk (Qing et al., 2015; Han et al., 2018).

The incremental lifetime cancer risk is assessed by the total cancer risk (ILCR) values of toxic metal(loid)s, which is the product of the lifetime average daily exposure doses (LADD) and its corresponding slope factor (SF). The ILCR is calculated as Eq. (10).

$$ILCR = LADD_i \times SF_i \quad (10)$$

If the values of ILCR are >10^{-4}, it indicates potential risk of cancer exists seriously; if ILCR is lower than 10^{-6}, it means no significant risk caused by carcinogens; if ILCR between 10^{-6} and 10^{-4}, it means probability of the adverse health effects (Wu et al., 2015; Han et al., 2018). The parameters applied for arsenic were showed in Table S2.

2.5. Statistical analysis

Data processing was conducted with Microsoft Excel 2016. Statistical analysis was performed using the SPSS statistical package (version 18.0 for Windows, SPSS Inc., USA), and all plots were drew by Origin (version 8.5 for Windows, Origin Lab Corp., USA). The distribution of toxic metal(loid) contents, and pollution indices were analyzed using ArcMap 10.2 with Kriging spatial interpolation method.

Principal component analysis (PCA), was used to determine the relationship among toxic metal(loid)s in soils and their possible sources (Facchinelli et al., 2001). The PCA of a small set of data, together with other information, could provide valuable insights into the sources of soil pollutants (Borůvka et al., 2005). And the strong correlations among toxic metal(loid)s potentially indicate their common origins and similar pathways and can be used to appraise the homogeneity of the sources of toxic metal(loid)s investigated (Li et al., 2017; Soliman et al., 2017). The KMO and Bartlett tests were conducted prior to PCA because these tests (KMO>0.05; Sig<0.05) can indicate whether PCA is useful for dimensionality reduction (Wang et al., 2015).

3. Results and discussion

3.1. Geochemical distribution of toxic metal(loid)s in local soils

The geochemical contents (e.g. maximum, minimum, average) of toxic metal(loid)s (Cu, Cr, Ni, Zn, Sb, Pb, Cd, Tl, As, Hg) in local soil samples were summarized in Table S3. Compared to the permissible levels for metal(loid)s in farmland soils of China, the contents of Tl, Cu, Hg and As in local soils generally exceeded the MPL (Maximum Permissible Level) for agricultural soils in China (SEP and GAQIQ, 2015; MEE and SAMR, 2018), which were consistent with our previous research results (Xiao et al., 2004a). The levels of other metal(loid)s (Cr, Ni, Zn, Sb and Cd) in local soils were also concentrated. All the metal(loid) levels in local soils were higher than their corresponding background values (CEMS, 1990; Wang et al., 1995). The concentration of Pb was overall within the trigger limit. The concentrations of Tl, As and Hg in local soils surpassed their corresponding permissible values 132 (Tl), 3.9 (As) and 111 (Hg) times from the mine area, respectively, and 11 (Tl) and 8.9 (Hg) times from the peripheral area, and 2.8 (Tl) and 1.8 (Hg) times from the undisturbed natural area. Overall, Tl, Hg and As were the major metal(loid) pollutants in local soils.

Thallium showed extremely high concentrations in local soils, i.e. 1.8 to 447 mg/kg (average at 77 mg/kg) from the mine area, 0.31 to 62 mg/kg (average at 6.5 mg/kg) from the peripheral area, and 0.38 to 19 mg/kg (average at 2.9 mg/kg) from the undisturbed natural area, respectively. All the averaged values for soil Tl were obviously higher than the background values for soils in China (0.58 mg/kg) (Qi et al., 1992), and as well in Guizhou Province (0.712 mg/kg) (CEMS, 1990). The Tl levels in local soils all highly exceeded the critical trigger limit of Tl regulated for agricultural soils in China (1 mg/kg) (SEP and GAQIQ, 2015). The results also figured out that 100% of samples from the mine area, 88.2% from the peripheral area and 73.3% from the undisturbed natural area, showing Tl levels exceeding the China soil MPL. In addition, Tl concentrations in the Lanmuchang area generally exceeded those in other areas of the world and China, such as high Tl contents at 1.54–55 mg/kg in the arable soils of France (Tremel et al., 1997), 8.8–27.8 mg/kg in soils from Silesian–Craeowian zinc–lead mine areas (Lis et al., 2003), 3.5–30.1 mg/kg in an organic horizon of forest soil profile from the Olkusz district, Silesia-Krakow region (southern Poland) (Vaněk et al., 2013), 3.17–4.47 mg/kg in soils from a Tl-rich pyrite mineralized zone in Eastern China (Zhou et al., 2008). The elevated Tl contents revealed that Tl was highly enriched in local soils that were derived from the mine wastes, slope-wash materials, alluvial deposits, undisturbed natural soils and background soils (Xiao et al., 2004a). This clearly suggested that the local agricultural soils were seriously contaminated with Tl.

Mercury was also highly enriched in local soils. About 99.3% of samples from the mine area, 70.6% from the peripheral area, and 50% from the undisturbed natural area showed Hg levels exceeding the China soil Hg MPL. The Lanmuchang area experienced historic sporadic mining activities for Hg for >350 years. Thus, the local past mining activities contributed to the elevated Hg in local soils. The total Hg contents (0.38–17 mg/kg, average at 3.2 mg/kg) in the undisturbed natural area were much higher compared to the world soils (0.01–0.5 mg/kg) (Senesi et al., 1999), and suggested that the natural sulphide mineralization in Lanmuchang area influenced the geochemical distribution of Hg in natural soils (Qiu et al., 2006). High Hg deposition flux was also found up to 1502 ng/(m^2 h) (Wang et al., 2005) in the study area. Hence, the enhanced Hg concentration in local natural soils also might imply for atmospheric deposition.

Arsenic concentrations in local soils from the mine area ranged from 1.7 to 616 mg/kg with an average at 156 mg/kg, higher than the China soil As MPL. The mean concentrations of As in the peripheral area and undisturbed natural area were both below the MPL of As, but exceeded the background values in soils in Guizhou Province and China. Thus, As also showed high enrichment in local soils from the MA and PA.

The content distributions of toxic metal(loid)s in local soils under different land use type showed significant variations (Fig. 2). The average concentrations of Tl, As and Hg in soils of the forest/grass land were observed significantly higher than other land use types in the mine area, and their concentrations in grain land were higher than those in vegetable land. This specific distribution implied for the contribution of local sulphide mineralization for Tl, As and Hg, in addition to disturbance of local past sporadic mining activities. In the peripheral area surrounding the mine site, the average concentrations of Tl, As and Hg in forest/grass land were lower than those in other lands. The local grain land and vegetable land are mainly along the local Qingshui Stream, and the soil matrices are derived from the alluvial deposition from the upstream sulphide mineralized zone. In addition, the local stream water is also rich for Tl, Hg and As, and the agricultural irrigation may also elevate the contents of toxic metal(loid)s in local framing land (Xiao et al., 2003; Qiu et al., 2006). For the undisturbed natural soils, the mean concentrations of Tl, Hg and As were still at a slightly higher levels, and were in consistent with the previous results (Qiu et al., 2006; Jia et al., 2013), which were attributed to secondary enrichment of the toxic metal(loid)s in local natural soils impacted by local sulphide mineralization (Xiao et al., 2004a).

3.2. The enrichment factors of toxic metal(loid)s in soils

The EF values of toxic metal(loid)s (Tl, Hg, As and Sb were herein chosen for assessed) in soils with different land use were plotted in Fig. 3, and their EF values from different areas were summarized in Table S4. The EF values ranged from 1.8 to 1055 (mean at 126) for Tl, 0.05–60 (mean at 9.4) for As, 4.1–16,555 (mean at 2248) for Hg, and 0.09 to 34 (mean at 4.0) for Sb, respectively, in soils from the sporadic mine area, whereas the EF values for Cr, Ni, Zn, Pb and Cd were generally below 2. Among them, As, Hg and Tl showed significant enrichment, due to the past sporadic mining for the sulphide minerals of cinnabar, orpiment and lorandite (Xiao et al., 2004a). The mean EF values of Cu, Cr, Ni, Zn, Pb and Cd were close to 1 in all land use types in the mine area, implying for geogenic origin. The mean EF values of Tl and Hg were larger than 10 in all land use types, but As EF values larger than 10 were only from the forest/grass land.

The EF values ranged from 0.32 to 70 (mean at 7.1) for Tl, 0.23–3.6 (mean at 1.3) for As, 0.78–53 (mean at 6.1) for Sb, and 2.6–909 (mean at 113) for Hg in the soils from the peripheral area, whereas the EF values of Cr, Ni, Zn, Pb, Cd and As were generally below 2. Among them, the peripheral area is covered by grain land and vegetable land, mainly along the local Qingshui Stream, and the soil matrices are derived from the alluvial deposition from the upstream sulphide mineralized zone. The mean EF values of Cu, Cr, Ni, Zn, Pb, Cd and As were close to 1 in all land use types, suggesting for geogenic origin. The mean EF values of Tl in the vegetable land and grain land, Hg in all land types were large than 2, implying for additional impacts of past sporadic mining activities. The toxic elements and their host minerals were enriched in the fine particles of the mine wastes, which could migrate through runoff and fluvial transport to the downhill farm lands (Xiao et al., 2004a).

For the background area, the EF values showed that Cr, Ni, Zn, Pb, Cd and As displayed slight enrichment in soils. The mean EF values of Sb in 30% of soil samples, Tl in 20% of soil samples were between 2 and 5, respectively, showing moderate enrichment. A small portion (13.3%) of soil samples showed significant enrichment for Tl. For Hg, most of the soil samples were at significant enrichment level, and 20% of the samples showed extremely high enrichment. The mean EF values of Cu, Cr, Ni, Zn, As, Pb and Cd were close 1 in all land use types, pointing to geogenic source. The EF values for Hg, Sb and Tl were larger than 2 in all land use types (Fig. 3), suggesting for secondary enrichment during the natural pedogenesis of local sedimentary rocks.

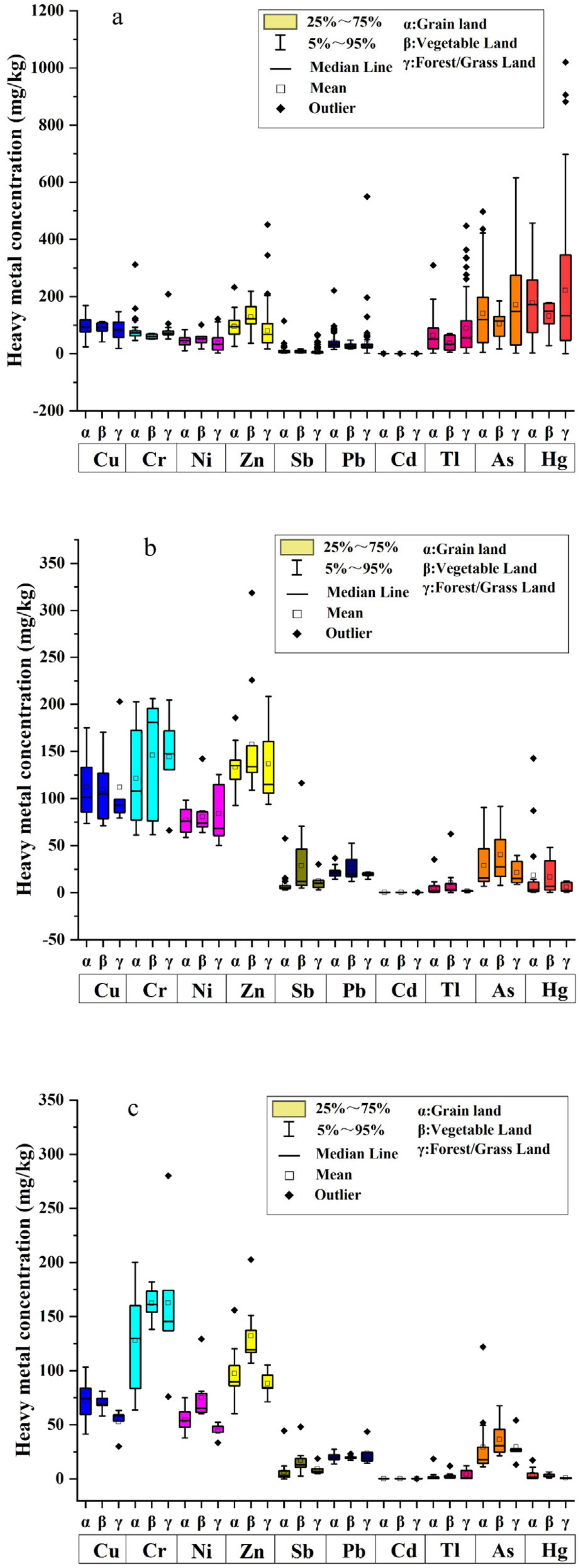

Fig. 2. Content distributions of toxic metal(loid)s under different land use. (a. Mine area; b. Peripheral area; c. Undisturbed natural area).

3.3. Source identification of toxic metal(loid)s in soils

In the present study, PCA was applied to discriminate the sources of toxic metal(loid)s in local soils. In the undisturbed natural area, the

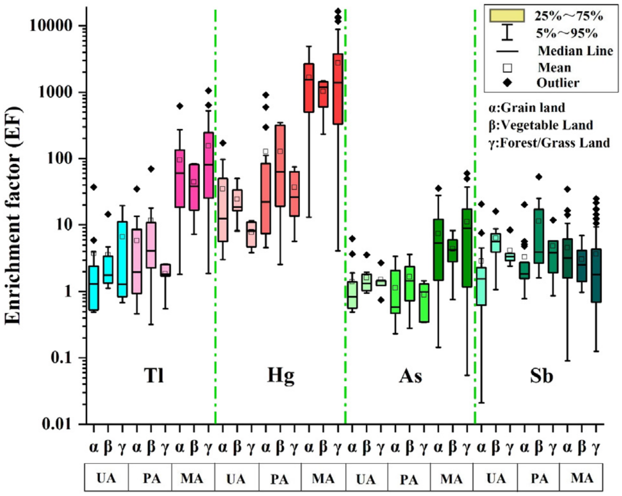

Fig. 3. Spatial distributions of Sb, Tl, As and Hg with significant EF values in local soils. (NA: Undisturbed natural area; PA: Peripheral area; MA: Mine area).

Kaiser-Meyer-Olkin measure of sampling adequacy (0.565) and Bartlett's test of sphericity ($p<0.001$) stated PCA suitability for the analysis of the data set. According to the PCA results, four groups had eigenvalues >1 (PC1–2.624; PC2–2.499; PC3–1.874; PC4–1.159). In the undisturbed areas, four factors extracted by PCA explained 81.557% of the total variance of the data. Varimax rotation of the four components were shown in Table 1. PC1 including Ni and Zn had strong positive loading, inferred the similar natural sources. Meanwhile, the mean EF values of Ni and Zn were close to 1, also suggested for geogenic origin. PC2 including As and Sb had strong positive loading and moderate positive loading of Pb, Sb and As, frequently co-occurring in sulphide minerals, and co-contamination of Sb and As is observed in some mining areas (Xiao et al., 2016). And the EF value of Sb exceeded 2, the two metalloids (As and Sb) supposed to have anthropogenic origin. PC3 including Hg had strong positive loading, moderate positive loading of Cu and strong negative loading of Cr, while the EF values of Cu and Hg were higher than 2, indicating that Cu and Hg derived from anthropogenic activities. PC4 including strong positive loading of Cd and moderate positive loading of Tl. Cd is considered as a marker of agricultural activities such as the use of pesticides and fertilizers (Lv et al., 2015), while EF value of Tl was higher than 2, suggesting for impact of past mining activities.

In the peripheral area, the Kaiser-Meyer-Olkin measure of sampling adequacy (0.441) and Bartlett's test of sphericity ($p < 0.001$) stated PCA suitability for the analysis of the data set. The PCA results showed that three groups had eigenvalues >1 (PC1–3.989; PC2–1.963; PC3–1.725), explaining 76.774% of the total variance of the data. Varimax rotation of the four components were shown in Table 1. PC1 including Pb, Tl, As and Hg had strong positive loading, suggesting for similar source. Also, the mean concentrations of these metal(loid)s exceeded their corresponding background values except for Pb, which could be inferred that they were sourced from anthropogenic origin, especially of the agricultural activities. PC2 including Ni, Zn and Sb had strong positive loading, the EF value of Sb >2, and suggested that they might have anthropogenic origin. PC3 including strong positive loading of Cr and moderate positive loading of Cd, strong negative loading of Cu, and the EF values of Cd and Cr were below 1, implying for source of both geogenic origin and anthropogenic impacts.

In the mine area, the Kaiser-Meyer-Olkin measure of sampling adequacy (0.561) and Bartlett's test of sphericity ($p < 0.001$) stated PCA suitability for the analysis of the data set. The PCA results showed that four groups had eigenvalues >1 (PC1–3.097; PC2–1.917; PC3–1.436; PC4–1.265), explaining 77.158% of the total variance of the data. Varimax rotation of the six components were shown in Table 1. PC1 including Tl, As and Hg had strong positive loading, suggesting for similar source, i.e. association with natural weathering of sulphide minerals (Xiao et al., 2004b). Also, the mean concentrations of these metal(loid)s exceeded their corresponding background values, which could be inferred that they were also impacted by the past sporadic mining activities. PC2 including strong positive loading of Cu, Ni and Zn, with EF values o close to 1, suggested for geogenic origin. PC3 including strong positive loading of Cr and Sb, with EF value of Sb larger than 1, suggested for similar source of mining activities. PC4 including strong and moderate positive loading of Pb and Cd, with EF values close to 1, suggested for geogenic origin.

Furthermore, the spatial distribution patterns of toxic metal(loid)s in local soils were mapped in Fig. S1. It's worth noting that the distributions of Tl, Hg and As were particularly concentrated in the mine area, indicating that the past sporadic mining was the main contribution source. Historical mining activities left behind a legacy of contaminated mine dumps, which may serve as a permanent source of Hg for the environment (Hojdova et al., 2008). However, the three metal(loid)s tended to disperse, resulting in enrichments in local surrounding areas. The distribution trends of Tl, Hg and As were quite similar, indicating the three metal(loid)s derived from the same sources, i.e. sulphide mineralization and past sporadic mining impact. The distribution of Cu, Zn, Ni, Sb and Cr showed that there might exist more than one pollution source, and further source apportionment analyses are required to quantify effects of different sources.

3.4. Ecological risk assessment

In this study, the RI data was applied to assess the degree of toxic metal(loid)s contamination in local soils. The calculated RI values of

Table 1
Factor loadings for varimax rotated PCA of toxic metal(loid)s in local soils.

Undisturbed natural area					Peripheral area				Mine area				
Toxic metal(loid)s	Component				Toxic metal(loid)s	Component			Toxic metal(loid)s	Component			
	1	2	3	4		1	2	3		1	2	3	4
Cu	0.469	−0.317	**0.661**	−0.409	Cu	0.243	0.518	**−0.777**	Cu	−0.103	**0.842**	0.042	−0.067
Cr	0.297	0.063	**−0.771**	−0.283	Cr	−0.174	0.206	**0.859**	Cr	−0.153	0.021	**0.893**	−0.123
Ni	**0.947**	0.073	−0.12	−0.024	Ni	−0.124	**0.902**	−0.094	Ni	−0.263	**0.846**	0.060	−0.008
Zn	**0.912**	0.206	0.159	0.023	Zn	0.483	**0.777**	0.033	Zn	−0.07	**0.726**	0.029	0.571
Sb	0.347	**0.852**	−0.075	−0.017	Sb	0.308	**0.701**	0.421	Sb	0.218	0.081	**0.843**	0.203
Pb	−0.380	**0.532**	0.245	0.474	Pb	**0.776**	0.365	−0.095	Pb	0.140	0.114	0.005	**0.833**
Cd	0.174	−0.217	0.058	**0.874**	Cd	0.330	0.039	**0.553**	Cd	−0.379	−0.317	0.082	**0.542**
Tl	−0.263	0.459	0.124	**0.562**	Tl	**0.883**	0.184	0.087	Tl	**0.830**	−0.042	0.064	−0.056
As	0.090	**0.909**	0.052	−0.074	As	**0.83**	0.141	0.167	As	**0.919**	−0.156	0.042	0.114
Hg	0.123	0.213	**0.848**	0.054	Hg	**0.839**	−0.146	−0.224	Hg	**0.872**	−0.285	−0.064	−0.046
Eigenvalue	2.624	2.499	1.874	1.159	Eigenvalue	3.989	1.963	1.725	Eigenvalue	3.097	1.917	1.436	1.265
Variance, %	26.243	24.988	18.739	11.587	Variance, %	39.889	19.631	17.254	Variance, %	30.974	19.171	14.359	12.653
Cumulative,	81.557%				Cumulative,	76.774%			Cumulative,	77.15%			

Extraction method: principal component analysis. Rotation method: Varimax with Kaise. In bold: strong (> 0.7) and moderate (0.5–0.7) loadings.

toxic metal(loid)s in soils under different land use type were plotted in Fig. 4.

The E_r^i values for single metal(loid)s decreased in severity in the order of Hg>Tl>As>Sb>Cd>Cu>Pb>Ni>Cr>Zn in the mine area. The ecological risks posed by Hg and Tl were quite high (E_r^i>320) for most sampling sites (98.7% and 88.9%), and the level of As presented considerable risk for 33.9% of the sampling sites. Other metal(loid)s revealed single risk indices below 40, which was indicative of low risk. Overall, the ecological risks posed by Hg, Tl and As in soils in the mine area were at a high level independent of land use type, due to both the intensive sulphide mineralization and past sporadic mining activities. According to the statistical results, 100% of the sampling sites presented quite strong risk (RI ≥ 600). Apparently, Hg and Tl dominated the two major risk sources because of high toxicity coefficient, with ratios of 94.2% and 5.6%, respectively (Fig. 5a). The potential ecological risk in different land use type followed the order of forest/grass land>grain land>vegetable land (Fig. 5b), and forest/grass land had a higher ecological risk in soils in the mine area.

The E_r^i values for single metal(loid) decreased in severity in the order of Hg>Tl>Sb>Cu>As>Cd>Ni>Pb>Cr>Zn in soils in the peripheral area. The ecological risks posed by Hg and Tl were very high (E_r^i>320) for most sampling sites (88.2% and 29.4%), and Tl presented considerable risk for 29.4% of the sampling sites. Other metal(loid)s revealed single risk indices below 40, which was indicative of low risk. Overall, the ecological risks posed by Hg in soils in the peripheral area were at a high level independent of land use type, and the ecological risks caused by Tl were at high level in the vegetable land and grain land, which were consistent with the results of the EF values. According to the statistical results, 79.4% of the sampling sites presented quite strong risk (RI ≥ 600), and Hg and Tl were the two main risk sources because of high toxicity coefficient with ratios of 92% and 6%, respectively (Fig. 5a). The potential ecological risks in grain land and vegetable land were much higher than that in forest/grass land.

As for the undisturbed natural areas, the mean E_r^i values of Tl and Hg were 160.3 (high risk) and 1146.9 (very high risk), respectively. Values of other metal(loid)s were below 40, revealing for low risk levels. According to the RI results, 66.7% of the sampling sites presented quite strong risk (RI ≥ 600). Soils in grain land and vegetable land posed higher potential risks than forest/grass land soils. Mercury and Tl were still the main risk sources in local soils.

3.5. Health risk assessment

Soil metal(loid)s threat human health through three main pathways, i.e. direct ingestion, inhalation of dust particles through mouth and nose, and dermal adsorption by skin exposure. Health risk assessment of non-carcinogenic metal(loid)s (combining three exposure pathways) for adults and children was illustrated in Fig. S2 and Tables S5–7. The results showed that the metal(loid)s except for Tl, Hg and As did not threaten the health and safety of adults and children in the mine area. The mean values HIs of Cu, Cr, Ni, Zn, Sb, Pb and Cd were all below the safety threshold. The mean His of Tl, As and Hg in the mine area were above the safe limits, presenting potential risk to children and adults. The HQ levels for different exposure pathways of toxic metal(loid)s were in the order of ingestion > dermal contact > air inhalation for Tl and As, whereas the order for Hg was dermal contract > ingestion > air inhalation. Compared to ingestion and dermal contact, the effect of air inhalation through the mouth and nose was negligible and quite unlikely to pose any significant risk (Tang et al., 2017). The risk levels of non-carcinogenic of toxic metal (loid)s to children were higher than adults, indicating that children are more sensitive and vulnerable to toxic metal(loid)s exposures. Children are more likely to contact with toxic metal(loid)s by inadvertent ingestion, such as pica behaviour and hand or finger sucking (Mielke et al., 1999). Moreover, children may contact much more toxic metal(loid)s during their outdoor play activities (Karim and Qureshi, 2014). Besides, the risk of toxic metal(loid)s is closely related with the valence states and the proportion of free state, such as Tl(I), As(III) and Hg(Me-Hg) (Feng et al., 2008; Li et al., 2012b; Xiao et al., 2018). By calculation, the highest incremental lifetime cancer risk of As was found from ingestion (Fig. S3, Table S8). All the mean values of ingestion in the mine area were higher than 10^{-4}, indicating serious potential risk. The mean values of dermal fell within the warning range of 10^{-6} to 10^{-4}, pointing to a tolerable level but necessary remediation needed. The ILCR of As exposed by air inhalation was within the range of safety. The descending order of ILCR via different pathway was the same as the HQ, for which ingestion was predominant, followed by dermal and air inhalation.

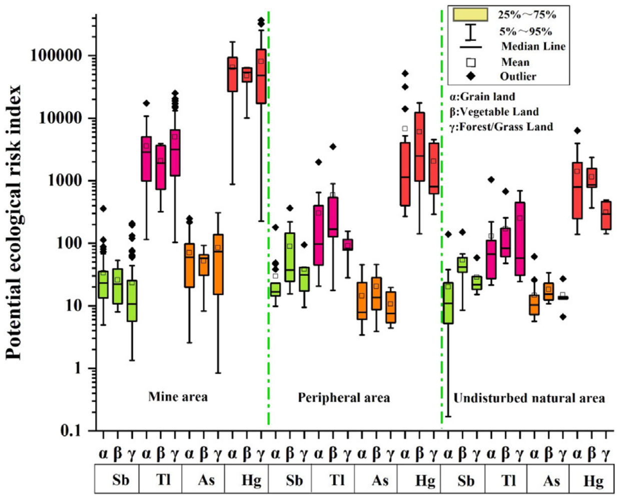

Fig. 4. Spatial distributions of Tl, As, Sb and Hg with significant E_r^i values in local soils.

The toxic metal(loid)s except for Tl did not threaten the health and safety of adults in the peripheral area, and Cr, Ni, Tl, As and Hg have potential risk to children. The mean values HIs of Cu, Zn, Sb, Pb and Cd were below the safety threshold. The risk levels of non-carcinogenic toxic metal(loid)s to children were higher than adults, indicating that children are more sensitive and vulnerable to toxic metal(loid)s. The mean HIs of Tl, As, Ni, Cr and Hg in the peripheral area were above the safe line for children as well as Tl for adults. The HQ levels to adults and children for different exposure pathways of toxic metal(loid)s were in the order of ingestion > dermal contact > air inhalation for Tl, as well as As to children. The HQ levels to children for different exposure pathways of Cr, Ni and Hg were in the order of dermal contact > ingestion > air inhalation. By calculation, the highest incremental lifetime cancer risk of As was found by ingestion (Fig. S3; Table S8). All the mean values of ingestion and dermal in the peripheral area fell within the warning range of 10^{-6} to 10^{-4}, indicating probability of the adverse health effects. ILCR of As exposed by air inhalation was within the range of safety. The descending order of ILCR via different pathway was the same as the HQ, for which ingestion was predominant, followed by dermal and air inhalation.

The toxic metal(loid)s, except for Tl, did not threaten the health and safety of adults in the undisturbed area, but Cr, Tl and As had potential risk to children. The mean values HIs of other metal(loid)s were below the safety threshold. The risk levels of non-carcinogenic toxic metal(loid)s to children were higher than adults, indicating that children are more sensitive and vulnerable to toxic metal(loid)s. The mean HIs of Tl, As and Cr in the undisturbed area were above the safe limits for children, as well as Tl for adults. The HQ levels to adults and children for different exposure pathways of toxic metal(loid)s were consistent with the other two areas. The highest incremental lifetime cancer risk of As was found from ingestion (Fig. S3; Table S8). The results of the calculation in the undisputed area was consistent with those from the peripheral area.

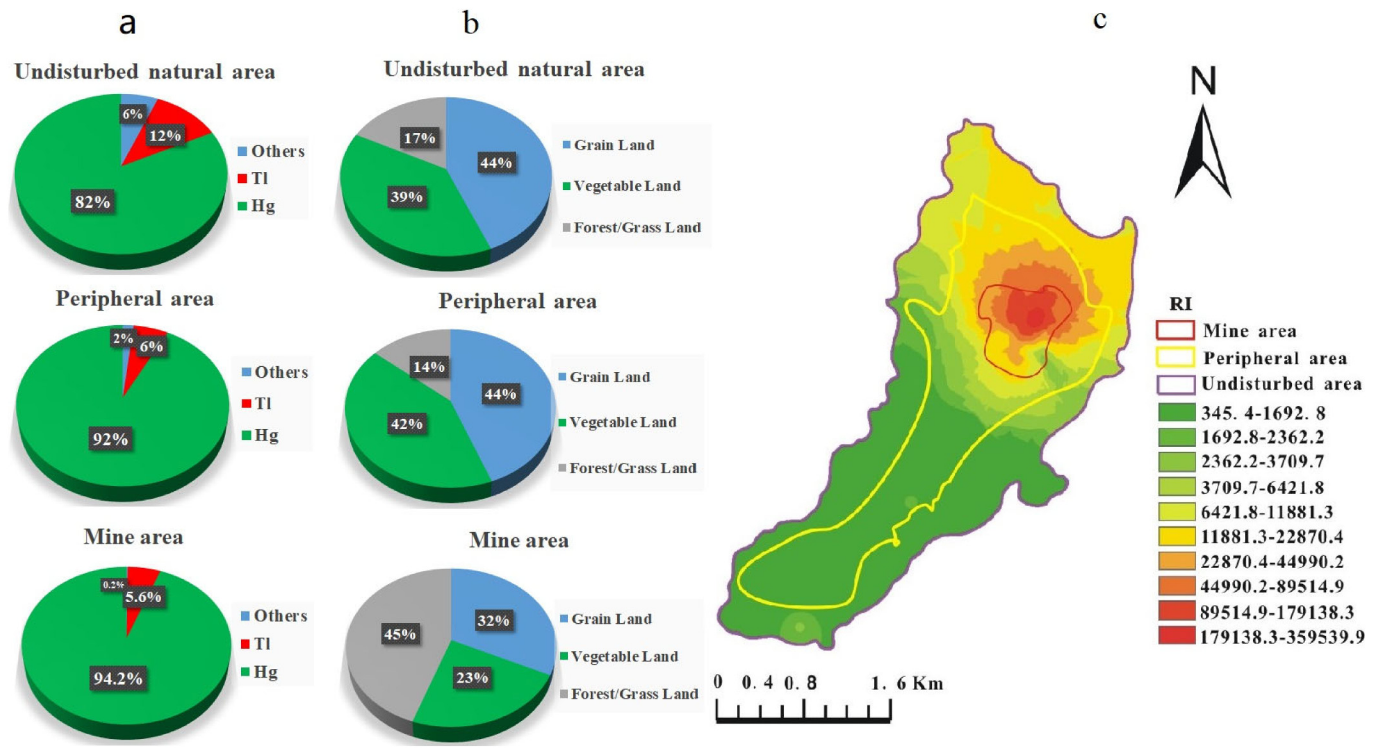

Fig. 5. a. The contribution of different elements to soil risk index; b. Soil risk index under different land use types in different areas; c. Soil ecological risk distribution in the whole study area.

4. Conclusions

Various analysis methods were apllied to identify the pollution characteristics, pollution sources and the health risks of toxic metal(loid)s in soils of the Lanmuchang area in southwest China. Tl, Hg and As are the three major toxic metal(loid)s with sinificant contamination in local soils, maninly due to the natural weathering of sulphide mineralization and historic sporadic mining activity. Pollution and health risk of Tl, Hg and As in local soils were exacerbated with the process of local sporadic mining and agricultural activities. Hg and Tl pollution in soils of the mine area impacted by past mining activities posed high ecological risk. High contents and enrichment of Tl and Hg in forest/grass land, where less human activities existed, had a greater impact on the ecological risk in the mine area, whereas Tl and Hg in the grain land and vegetable land, where more agricultural activities existed, dominate soil ecological risk in the peripheral area. Both children and adults faced non-carcinogenic potential exposure risk of Tl, Hg and As in soils in the mine area. The toxic metal(loid)s of Cr, Ni, Tl, As and Hg had non-carcinogenic potential risk to children and non-carcinogenic potential risk of Tl to adults in the peripheral area. Cr, Tl and As had non-carcinogenic potential risk for children and Tl presented non-carcinogenic potential risk for adults in the undisturbed natural area. Children were more sensitive and vulnerable to toxic metal(loid)s than adults. The exposure pathway analysis figured out that non-carcinogenic exposure risk was mainly through ingestion of Tl and As and dermal contract of Hg in the mine area, ingestion of Tl and As and dermal contract of Cr, Hg and Ni in the peripheral area, and ingestion of Tl and As and dermal contract of Cr in the undisturbed natural area. Arsenic in soils presents high carcinogenic exposure risk through ingestion of soil particles in the mine area, probability of the adverse health effects through ingestion of soil particles in both the peripheral area and the undisturbed natural area. This study expounds the reality of the soil pollution status and potential hazards caused by toxic metal(loid)s under difference land use, and the fingdings` would be helpful for local soil pollution remediation and land use management.

CRediT authorship contribution statement

Liang Ma: Investigation, Methodology, Formal analysis, Writing - original draft. **Tangfu Xiao:** Writing - review & editing, Conceptualization, Supervision. **Zengping Ning:** Writing - original draft, Project administration. **Yizhang Liu:** Writing - original draft, Data curation. **Haiyan Chen:** Data curation, Formal analysis, Investigation. **Jingquan Peng:** Investigation, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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