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Transfer processes of potentially toxic metals (PTMs) between rock–soil systems and soil risk evaluation in the Baoshan area, Yunnan province, Southwest China

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Highlights:

* Geochemical flux of rock–soil from different geological formations were revealed

- 23 * The geochemical flux indicates a lithological origin for PTMs
- 24 * I_{geo} and EF may underestimate PTMs contamination in high geological background areas
- 25 * Geochemical background values should be proper chose when calculate
- 26 * Mining activities contributions to soil contaminations of PTMs near the mining
- 27 areas

28 Abstract

29 Geochemical fluxes in rock-soil systems are an important tool to evaluate soil
30 environmental risk, especially where the geological background (parent materials)
31 are enriched in potentially toxic metals (PTMs). In the Baoshan area, the presence
32 of mineral resources and carbonate and basalt parent materials often leads to PTMs
33 being elevated in soils. In this study, we compared rock and soil geochemical
34 compositions by collecting rock samples from the host formations and ore samples
35 from two mineral deposits (Cu-Pb-Zn and Fe-Cu-Pb-Zn) and their overlying soils. This
36 research demonstrates enrichment of PTMs (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) in soils
37 relative to their parent materials. The enrichment in soils may be due to the removal
38 of mobile elements (e.g., Ca, Na, Mg, and Sr), and coprecipitation (As, Cd, Cr, Cu,
39 Hg, Ni, Pb and Zn) and/or adsorption by Fe-oxy-hydroxides (Cr and Ni) under the
40 influence of high pH values during soils formation. The results point to a parent
41 lithological origin and natural enrichment of PTMs in Baoshan soils. However,
42 anthropogenic contamination of soils near mining areas is also possible. Soils
43 forming from carbonate rocks, basalts, and especially from mineralized formations

have higher PTMs concentrations, and in places, levels can exceed the risk screening values for soil contamination of agricultural land of China. Where the latter is the case, it is suggested that ecological monitoring be implemented in the study area. The geo-accumulation index (I_{geo}) and enrichment factor (EF) methods used may underestimate the PTMs contamination, and comparison with larger-scale background datasets when calculating results may be a better way to evaluate soil environment risk in high geological background areas.

Keywords: Potentially toxic metals (PTMs); Rock-soil systems; Geochemical fluxes; Geo-accumulation index (I_{geo}); Enrichment factor (EF); Southwest China

1. Introduction

Soil sustains all terrestrial organisms and is the medium for all biogeochemical processes. However, it is a finite resource that is not renewable on a human time scale (Purswani and Pathak, 2018). With competing pressures between population, resources and environment, soil quality has become a major concern globally (Antibachi et al., 2012; Cheng et al., 2014a; Cheng et al., 2014b; Cheng et al., 2014d; Cicchella et al., 2008; Gong et al., 2014; Li et al., 2010; Li et al., 2014b; Luo et al., 2012; Zhang et al., 2013). Source of potentially toxic metals (PTMs) are most often considered to be anthropogenic in origin (e.g. industrial and mining activities, agricultural fertilization, and irrigation and urban living pollutants). Such sources have been recognized by public authorities and well researched by scientists. (Addo et al., 2012; Akopyan et al.; Cabral Pinto et al., 2018; 2019a;

2019b; Chiu et al., 2016; Ettler, 2016; Hamzeh et al., 2011; Li et al., 2014b; Luo et al., 2012; McGrath and Tunney, 2010; Pinto et al., 2004; Poňavič et al., 2018; Rate, 2018). Soil can be naturally contaminated due to release of PTMs from parent materials during weathering and this is evidenced by a significant body of research in this field e.g. (Antibachi et al., 2012; Becquer et al., 2006; Bompoti et al., 2015; Bonifacio et al., 2010; Kelepertzis et al., 2013; Tashakor et al., 2014). Therefore, it is crucial to understand geochemical fluxes rock-soil systems, especially where the geological background (parent materials) are enriched in PTMs. Understanding these fluxes will provide an important tool for assessing the natural environmental/ecological risk to soils. In this study, we examine geochemical fluxes at a regional scale. This has been achieved through the collection of rock samples from the host rock sequences, ore samples from two mineral deposits (HTTP: Cu-Pb-Zn and HYA: Fe-Cu-Pb-Zn), and samples from overlying soils. In this and other areas, the presence of carbonate and basalt parent materials often leads to elevated PTMs in soil (Barsby et al., 2012; Cabral Pinto et al., 2017; Cheng, 2016; Cox et al., 2017; Goldhaber et al., 2009; Tolosana-Delgado and McKinley, 2016; Wang et al., 2015; Zhang et al., 2002).

Statistical analysis of geochemical data from different geological formations and their overlying soils was used to (1) reveal the concentration of PTMs in the rock-soil systems in the study area, (2) evaluate the enrichment and depletion of PTMs in soils related to their underlying rock formations, (3) understand the transfer processes of PTMs from rocks to soils, and (4) evaluate ecological risk

and provide ecological risk prediction to similar geological areas.

2. Research area

The Baoshan area is located in southwest China in the Yunnan province (Fig. 1a). The area has a mild subtropical that is tempered by its low latitude and moderate elevation. Baoshan has short, mild, dry winters, and warm, rainy summers. Contour maps of altitude, average surface soil temperature and rainfall are shown in Fig. 2. Variations in average temperature are directly related to altitude, whilst rainfall is greatest in the western and southern parts of the study area. The main types of land-use in the study area are forested land, dry cultivated land, paddy land, grassland, garden plot, with few water areas and other types (residential quarter and industrial and mining land, and unused land) (Fig. 3a). The main soil types in the study area are red soils, yellow red soils, yellow crimson red soils, dry red soils, yellow brown soils, dark yellow brown soils, paddy soils with few brown soils, acid purple soils and other types (Fig. 3b).

Geologically, the area is located in the Sanjiang area of the Yunnan province, which consists of the Tengchong, Baoshan, and Lanping-Simao blocks (Fig. 1b) (Dong et al., 2013; Li et al., 2015; Wang et al., 2010). Rocks 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). From the Precambrian to Quaternary, the main rock type for each era is shown in Fig. 4. Basalt occurs in the Carboniferous and Jurassic rock sequences that are mainly

distributed in the western and northeast parts of the study area. Whilst mineral deposits, which are often associated with PTMs pollution in soil, are widely distributed across the study area (copper, lead, zinc, mercury, gold, titanium and coal, etc.,) (Fig. 4).

3. Methodology

3.1 Sampling methods

An area of 6220 km² of the 2016 National Geochemistry Survey of Land Quality project (NGSLQ) was selected as the research area because of the range of bedrock geology and mineralization present. Samples of bedrock from all the main rock groupings and their overlying soils were collected. Additionally, ore samples from two deposits (the Hetaoping copper-lead-zinc deposit (HTP) and Heiyanao iron-copper-lead-zinc deposit (HYA)) and their overlying soils were also taken.

The sampling locations did not follow a predetermined criterion, as their selection required finding bedrock outcrops with or without mineralization and overlying soil. In total 102 rock samples from 9 geological formations, including 20 rock samples from the two basalt formations (Carboniferous and Jurassic), and 20 mineralized samples were collected. The sample details are provided in Table 1. Corresponding surface soil for each rock/ore sample, at 0–20 cm depth, were collected. Soil samples were composited from 3 to 5 subsamples collected within 50 m of each bedrock sample site. Soil samples were ≥ 1 Kg, and visible plant detritus and rock fragments were removed during collection. The detailed soil type, soil

characteristic, parent rocks/formations, and sample numbers are showed in [Table 2](#). All the sampling positions were pinpointed by the Global Positioning System (GPS). The sample locations are shown in [Fig. 5](#).

Obvious mineral veins material was removed from the rock samples. Ore samples and the remainder of rocks were grounded using an agate mortar to -200 mesh (<0.074 mm) for analysis. The soil samples were disaggregated using a wooden hammer during air-drying and sieved with -20 mesh screen (<0.84 mm), once dried they were further processed to -200 mesh (<0.074 mm) for total content analysis and -100 mesh (<0.25 mm) for extractable As, Cd, Pb analysis.

3.2 Chemical analysis and quality control

Rock/ore and soil samples were analyzed for total content by XRF (Al_2O_3 , TFe_2O_3 , K_2O , SiO_2 , Na_2O , MgO , CaO) after digestion by lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$); by XRF (Zr and Hf) after powder pressing; by ICP-OES (Ba, Ni, Sr, Cr,) and ICP-MS (Cd, Cu, Cs, Pb, Rb, Ta, Th, U, Zn and Nb), after digestion by hydrofluoric acid (HF), hydrochloric acid (HCl), nitric acid (HNO_3) and perchloric acid (HClO_4); by AFS (As, Hg) after digestion with aqua regia; by HFIR (S), add tungsten grain in high-frequency infrared carbon sulfur meter; by VOL (C.org) after digestion by potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and concentrated sulfuric acid (H_2SO_4); and by ISE (pH) after dissolved in CO_2 distilled water. Extractable As, Cd, Pb from soil samples were digested using calcium chloride (CaCl_2) and analyzed by AFS (As) and ICP-MS (Cd and Pb). The analysis finished at the Geological Experimental Testing Center,

Hubei province, China, which is one of the geological laboratories by accredited by the NGSQ project. The analytical methods brand and the model of analysis devices, and detection limits were listed in Table 3. Internal and external controls were implemented during routine analysis to check accuracy and precision. Briefly, certified reference materials (CRMs) and blind reference materials (BRMs) were analyzed with samples simultaneously to control the quality of sample analysis. The detailed description can be seen in (Li et al., 2014a). The accuracies and precisions of all elements in all samples satisfy the analytical requirements developed in the NGSQ project (CGS, 2005, 2014) and Code of Geochemical Rock Survey of China (Ministry of Land and Resources of the People's Republic of China, 2014).

3.3 Statistical analysis

Geochemical data are compositional data, in which the concentrations of each element are not changed independently and freely, but must accommodate to each other within the constant sum constraint of the closed composition. Which was identified to induce spurious behavior on the correlation coefficient (Chayes, 1960). Aitchison and his fellower researchers have developed the compositional data analysis methods to make the classical (Euclidean) statistical methods applied to compositional data available (Aitchison 1981, 1982, 1986; Egozcue et al. 2003; Boogaart and Tolosana-Delgado, 2013; Egozcue et al., 2003; Pawlowsky-Glahn and Buccianti, 2011; Pawlowsky-Glahn and Egozcue, 2001).

In this paper, centred log-ratio transformation (clr) are used in CoDAPack to

“open” the raw data, before statistical analysis. CoDAPack is a freeware package that implements most of the basic statistical methods suitable for compositional data (Thio-Henestrosa and Martin-Fernandez, 2006). Origin 2020 software was used for principal component analysis (PCA) on the log-ratio (clr) transformed data, using a correlation matrix, to determine the associations of chemical elements.

4. Results and discussion

4.1 Chemical characteristics of rocks and soils

4.1.1 Rocks

Within the study area, the formations are distinguished based on the main rock type and these differ for most of the formations. Average (median value) concentrations of chemical elements of rocks from different geological formations and ores of the Baoshan area are shown in Table 4. Formations with carbonate rocks as their main rock type (€-3, D, C, T-1, T-2, J), those with mudstone and sandstone as main rock types (€-1, €-2, O, S), and those with basalts in Carboniferous and Jurassic stratum (Ba-1 and Ba-2) and ores from mineral deposits all display different chemical characteristics.

The carbonate formations have higher median values of CaO and Sr and lower Al₂O₃, Fe₂O₃, MgO, SiO₂, Ba, Cr, Cs, Cu, Hf, Nb, Ni, Pb, Rb, Ta, Th, U, Zn and Zr compare to other formations apart from dolomite (T-2) which has the highest MgO content. Basalt formations have higher median values of Fe₂O₃, CaO, Na₂O, MgO, Cr, Cu, Ni and

Sr and lower Cs, Rb, Th, U contents compared to other formations. Mudstone and sandstone formations have higher median value of K₂O, SiO₂, Ba, Cs, Nb, Rb, Ta, Th, U and Zr and lower CaO and Sr. Ore samples from the HTP and HYA mining areas have the highest median values of Fe₂O₃, As, Hg, Cd, Cu, Pb, Zn, and S.

To identify geochemical associations between the elements analyzed in the rocks and ores, PCA was performed using the centred log-ratio transformed (clr) data. The numerical output with the eigenvalues ≥ 1 (PC1: 46.9% of variance, PC2: 19.1% of variance, PC3: 11.7% of variance, and PC4: 4.5% of variance) of principal components are listed in (Table 5), which captured potentially useful information. But only the first 3 principal components are examined here. The biplots of the principal components for the clr-transformed data of rocks and ores are shown in Fig. 6. With the aid of Table 5 and Fig. 6, the following observations have been made:

PC1 has the greatest positive contributions from As, Cd, Hg, Pb, Zn and S; and the strongest negative contributions from Al₂O₃, Cr, Hf, Nb, Rb, Ta, Th, and Zr. PC2 had great positive contributions from CaO, MgO and Sr; and strong negative contributions from TFe₂O₃, Cu and SiO₂. PC3 had great positive contributions from Cs, Rb, Th and U; and strong negative contribution from Na₂O.

Several approximate elemental associations can be seen from component loadings in PC1-PC2, and PC1-PC3 space: chalcophile element (Cu, As, Cd, Hg, Pb, Zn and S) occupied the +PC1/ $\pm$ PC2 quadrant (Fig. 6a). This group of elements is related to ore samples from HTP and HYA. It clearly shows the influence of mineralization and its typical ore minerals, such as galena (Pb, S), chalcopyrite (Cu, Fe, S),

sphalerite (Zn, S), pyrite (Fe, S), chalcopyrite (Cu, Fe, S) pyrrhotite (Fe, S), magnetite (Fe), hematite (Fe, O). Arsenic and Hg are accessory elements that accompany Cu-Pb-Zn mineralization. Cd normally replacement of Zn due to their analogous nature (Alvarezayuso and Garciasanchez, 2003). The lithophile elements Al_2O_3 , K_2O , SiO_2 , Ba, Hf, Nb, Ta, Th, Zr, Cs and Rb occupied the -PC1/ $\pm$ PC2 quadrant (Fig. 6a). It clearly shows the influence of mudstones and sandstones which are enriched in lithophile elements in lithologies. CaO , Sr, and MgO were grouped in the +PC1/+PC2 quadrant (Fig. 6a). Those elements are related to the carbonate formations (E-3, D, C, T-1, T-2, J), which are enriched in Ca, Sr and MgO (in T-2) compare to other rocks. The siderophile elements (Fe, Cr, Ni and MgO) occupied the -PC1/ - PC3 quadrant (Fig. 6b). It shows the influence of basalt, which enriched in siderophile elements contained minerals (such as pyroxene, olivine, amphibole, chromite, titanite, opaque minerals and serpentine) (Cabral Pinto et al., 2017).

4.1.2 Soils

The average concentration of chemical components in soils overlying the rocks of different geological formations and near HTP and HYA mining areas of the study area are showed in Table 6.

The soils near the HTP and HYA mining areas have the highest As, Cd, Cu, Hg, Zn and Pb concentrations compared to soils overlying other formations. The soils overlying carbonate rocks, also show those metals (As, Cd, Cu, Hg, Zn, Pb) enrichment. The soils overlying carbonate rocks in T-2 and J formations and soils overlying

basalt formations (Ba-1 and Ba-2), have higher CaO, Sr contents and pH value than seen for others. Conversely, soils overlying mudstone and sandstone formations (€-1, €-2, O, S) have lower CaO, Sr and pH compared to soil overlying other formations. The soils overlying basalt formations (Ba-1 and Ba-2) have higher TFe₂O₃, Na₂O, MgO, SiO₂, Cr and Ni. Soils overlying carbonate formations also show enrichment of Cr and Ni. The soils overlying €-1 and €-2 and near the HTP and HYA mining areas have higher organic carbon (C.org) than other soils, whilst no obvious difference of C.org was found among soils overlying other formations.

The numerical output with the eigenvalues ≥ 1 (PC1: 33.3% of variance, PC2: 27.2% of variance, PC3: 9.0% of variance, and PC4: 8.0% of variance, PC5: 6.27% of variance, PC6: 3.87% of variance) from the principal component of soil are listed in [Table 7](#). But only the first 3 principal components are examined here. With the aid of [Table 7](#) and [Fig. 7](#), the following observations were made:

PC1 has the greatest positive contributions from As, Cd, Cu, Pb and Zn; and the strongest negative contributions from Al₂O₃, SiO₂, Hf, Nb, Ta, Th, U and Zr. PC2 had great positive contributions from K₂O, Rb, Th and U; and strong negative contributions from CaO, TFe₂O₃, Na₂O, MgO, Cr, Ni, Sr and pH. PC3 had great negative contributions from Ba, S and C.org.

Several associations were apparent from component loadings plotted in PC1-PC2, and PC2-PC3 space: chalcophile element (Cu, As, Cd, Hg, Pb, Zn and S) occupied the +PC1/ $\pm$ PC2 quadrant ([Fig. 7a](#)). This group of elements is related to soil samples from near the HTP and HYA deposits and inherits the geochemical characteristics of

the ore. The lithophile elements Al_2O_3 , SiO_2 , K_2O , Ba, Hf, Nb, Rb, Ta, Th, U, Zr, Cs and Rb occupied the $-\text{PC1}/\pm\text{PC2}$ quadrant (Fig. 7a). It clearly shows the influence of sandstone and mudstone which are enriched in those lithophile elements and soils from carbonate formations (€-3, D, C, T-1) due to the coprecipitation of insoluble elements during weathering and soil formation processes. Siderophile element (Fe, Cr and Ni and CaO and MgO) and pH occupied the $\pm\text{PC1}/-\text{PC2}$ quadrant (Fig. 7a), which in one way are related to basalts, which are enriched in Fe, Cr, Ni, Mg, Ca compare to other rock types. The soils forming from basalts inherit the geochemistry characteristic of their parent material. The other way is due to the removal of mobile elements (e.g., Ca, Na, Mg and Sr) and the insoluble element (e.g., Cr and Ni) coprecipitation and/or adsorption by Fe-oxy-hydroxides under the influence of high pH values. The soils overlying carbonate formations J and T-2 are enriched in Cr and Ni due to that reason. Potentially toxic metals (PTMs) coprecipitation and/or adsorption by Fe-oxy-hydroxides during weathering and soil formation process was also found by other authors (Buccianti et al., 2015; Cabral Pinto et al., 2017; Caillaud et al., 2009; Hamon et al., 2004; Rate, 2018). Organics related elements (e.g., C.org, S, Ba) are related to soils forming from €-1 and €-2 formation and near the HTP and HYA mining areas. Fine-grain minerals in soils formed from mudstones are conducive to the accumulation of organic matters. Another reason could be that lower temperatures in these higher altitude areas limit organic turnover, which results in their increased accumulation even under conditions of smaller productivity of organic related elements input (Leifeld et al., 2005; Wiesmeier et

al., 2013).

4.2 Enrichment and depletion of PTMs in soils related to parent materials

Table 8 shows the enrichment and depletion of PTMs in the soils (S) overlying each geological formation and near the mining areas in relation to the bedrock (R), determined by S/R. Fig. 8 is presented to help to highlight the differences. Values <1 means that soils overlying a specific formation are depleted in PTM and values >1 mean that the soils are enriched. Soils overlying each geological formation, tend to be enriched in insoluble elements and depleted soluble elements related to the parent materials, and the amount of depletion is particularly significant in soils overlying carbonate formations (E-3, D, C, T-1, T-2, J). Soil compositions show slightly different enrichment and depletion trending to their parent rock in different formations.

Soils overlying basalts (Ba-2 and Ba-1) are enriched in K, As, Cd, Cs, Hg, Rb, S, Th and U; and depleted in Ca, Na, Mg and Sr. Whilst other elements do not show obvious enrichment or depletion. Soils overlying mudstone and sandstone formations (E-1, E-2, O, S) are depleted in K and Mg; and enriched in Ca, As, Cd, Hg, Pb and S. Soils overlying carbonic formations (E-3, D, C-1, T-1, T-2, J) are depleted in Ca, Na, Sr and Mg (in T-2); and enriched in nearly all other elements. The depletion of soluble elements such as Ca, Na and Sr are due to they have washed away during weathering. The enrichment in Hf, Nb, Rb, Ta, Th and U are due to their low mobility

during surface processes. While, the enrichment of Fe is due to its precipitation as oxy-hydroxides, whilst the enrichment of PTMs (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) in the soils may be resulted by their coprecipitation and/or adsorption by Fe oxy-hydroxides (Buccianti et al., 2015; Cabral Pinto et al., 2017; Caillaud et al., 2009; Hamon et al., 2004; Rate, 2018).

Soils near the HTP and HYA mines are depleted in Ca, Fe, Cd, Cu (in HTP), Hg (in HTP), Pb (in HTP), S and Zn. Again, the depletion of Ca is because it easily mobilized and tends to be washed away during weathering. The depletion of other minerals is apparent and due to their high concentrations in the ore samples. Soils overlying HTP and HYA are enriched in Al, K, Ba, Cr, Hf, Nb, Ni, Rb, Ta, Th, U, Zr due to their coprecipitation during weathering.

4.3 Risk evaluation

Soils with the values of PTMs (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) that exceed the risk screening values for soil contamination of agricultural land of the People's Republic of China (PRC) are listed in Table 9. If the concentration of PTMs in agriculture land is lower than or equal to the risk screening values, the ecological risk of soils and environmental quality of agricultural products grown on the land are low, whereas if the concentration of PTMs in agriculture land is higher than the risk screening values, the ecological risks for the soils and agricultural products grown in them. Where the later is the casing soil environmental monitoring and collaborative testing of agricultural products should be executed (Ministry of

Ecology and Environment of The People' s Republic of China, 2018).

Most of the soil samples with the PTMs values exceed the risk screening values are overlying the carbonate formations, basalt formations and near the HTP and HYA mining areas. For As, the samples mainly overlying €-3, C, T-1, T-2, HTP and HYA and with a few samples in €-1 and €-2. For Cd, the samples are mainly overlying C, T-1, T-2, HTP and HYA. For Cr, the samples are mainly overlying T-1, T-2, Ba-1 and Ba-2. For Cu, the samples are mainly overlying €-3, T-1, HTP, HYA and Ba-1. For Ni, the samples are mainly overlying €-3, C-1, T-1, T-2, Ba-1 and Ba-2. For Pb and Zn, the samples are mainly overlying €-3, HTP and HYA. Only two soil samples in study area are exceed the risk screening value of Hg, one overlies C-1, the other overlies €-3. As discussed previously, high levels of PTMs in soil overlying basalt formations (Cr, Cu, Ni), and near HTP and HYA (As, Cd, Cu, Pb, Zn) are due to their high concentrations in the bedrocks, whilst soils inherited their geochemistry characteristics from parent materials. For soils overlying carbonate formations high levels are due to the coprecipitation (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) and/or adsorption by Fe-oxy-hydroxides under the influence of high pH values (e.g. Cr and Ni). The soils sample forming on carbonate rocks, basalts and in mining areas have higher PTMs content and higher ecological risk which has also been found by other researchers (Barsby et al., 2012; Cabral Pinto et al., 2017; Cheng, 2016; Cox et al., 2017; Goldhaber et al., 2009; Tolosana-Delgado and McKinley, 2016; Wang et al., 2015; Zhang et al., 2002).

The index of geo-accumulation (I_{geo}) and enrichment factors (EF) which are used

widely to assess levels and origins of contamination (Barbieri, 2016; Bern et al., 2019; Cevik et al., 2009; Feng et al., 2011; Ghrefat et al., 2011; Liénard et al., 2014; Thiombane et al., 2019; Zhang et al., 2014). Reimann and Caritat (2000; 2005) and Sucharovà et al (2012) have proposed that these indices cannot be used as rigorous, objective or sensitive tools to detect or prove anthropogenic impact on the environment due to the flaws of EF and I_{geo} , these indexes are still considerable tools to assess levels of contamination their possible origins by choosing proper background values and comparing to other evidence.

The I_{geo} and EF are calculated using the following equations (Eq. 1 and 2):

$$(1) \ I_{geo} = \log_2 \left[\frac{C_n}{1.5B_n} \right]$$

where C_n is the concentration for a given PTM and B_n is the background level of that PTM in the soil (Müller, 1969). The median values of PTMs in deep soil from the 1:250000 scale land quality geochemical in Baoshan area, as are much less likely to be affected by human activities (Cheng et al., 2014c) and geochemical background baseline of China, the median values of deep soil of China Geochemical Baseline project (Wang et al, 2016) were used as B_n for calculation separately.

$$(2) \ EF = \frac{(Metal/RE)_{soil}}{(Metal/RE)_{rock}}$$

Where EF is the enrichment factor for a given PTM, subscript “soil” indicates surface soil concentration for that PTM, subscript “rock” indicates that PTM in the bedrocks, and “RE” is the concentration of reference element. Aluminum is choosing as RE for its non-mobile nature during weathering (Balls et al., 1997;

Cabral Pinto et al., 2017; Ryan and Windom, 1988; Sinex and Wright, 1988).

The results of I_{geo} with the value >2 are considered to be contaminated, according to previous studies (Müller, 1969; Odewande and Abimbola, 2008). The numerical results are shown in Table 9. The results of I_{geo} for Cd, Pb, Zn based on local background levels (median values of deep soil from the 1:250000 scale land quality geochemical in Baoshan area) and geochemical background baseline of China (the median values of deep soil of China Geochemical Baseline project) do not show much difference. The soils with As, Pb and Zn contamination occur mainly near HTP and HYA mining areas; the soils with Cd contamination mainly from the C, T-1 and T-2 formations and soils near HTP and HYA mining areas. While, for elements Hg, Ni and Cu show different results base on the B_n . Use local background as B_n may underestimate the PTMs contamination in where there is a high geological background of PTMs. By conducting a comparison with larger-scale datasets as background when calculating this is a better way to solve the problem.

Normally, the value of $0.5 < EF < 1.5$ is taken as an indicator that PTMs are entirely provided from natural contribution such as weathering, and a value of $EF > 1.5$ is considered to indicate the PTMs are delivered from non-crustal materials, for example, biota and/or pollution drainage (Zhang and Liu, 2001). Combine the contamination categories most authors used (Addo et al., 2012; Barbieri, 2016; Loska et al., 2003), soils with EF value >2 are thought to be moderately contaminated and caused by anthropogenic activities in this study. The results are shown in Table 9, show that, soils with As, Cd, Hg Pb contamination are mainly overlying formations

of €-1, €-2, 0, S and Ba-2. Those contaminate sample locations according to EF value are mainly near mining areas (Fig. 3), and this may indicate that the mining activities led to soil contamination. While no contamination was found in the soils near HTP and HYA mining areas according to EF results. This is due to the high concentration of PTMs (As, Cd, Hg, Pb, Zn) in ores. As such, the EF calculated for soil-rock in high geological background areas may underestimate the contamination.

Assessment the concentration of bioavailable of PTMs in soils is vital important in evaluate soil quality (Barbieri, 2016; Barsby et al., 2012; Cox et al., 2017; Jackson et al., 2016; Palmer et al., 2014; Prathumratana et al., 2018; Zhang et al., 2018). For the reason, PTMs in soil from anthropogenic origins tend to be more mobile, hence more bio-available than for pedogenic or lithogenic ones (Basta et al., 2005; Kuo et al., 1983; Nannoni et al., 2011). To find the biological risk of PTMs, the extractable Cd, Pb and As of soil samples were analyzed, the results are showed in Table 10. Extractable As is not discussed in this paragraph, due to their content in most of the soils being lower than detection limits. The soils overlying HTP and HYA have higher extractable Cd and Pb than other soils (Table 10), which may indicate the mining activities contributions to the surface soils contaminations near the mining areas.

Based on the soil environmental assessment methods used above, we suggest that the monitoring of soils formed on carbonate rocks and basalts, and especially mineralization formations and mining areas should be implemented in this study area.

5. Conclusions

This research demonstrates enrichment of potentially toxic metals (PTMs) (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) in soils related to their parent materials. The enrichment in soils may be due to the removal of mobile elements (e.g., Ca, Na, Mg and Sr), and coprecipitation (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) and/or adsorption by Fe-oxy-hydroxides (Cr, Ni) under the influence of high pH values during soils formation. However, anthropogenic contamination is also possible for soil near mining areas. The soils forming from carbonate rocks, basalts, and especially mineralization formations have a higher PTMs concentration, that exceeds risk screening values for soil contamination of agricultural land of China. Ecological monitoring should be implemented on those soils in the study area. The geo-accumulation index (I_{geo}) and enrichment factor (EF) methods may underestimate PTMs contamination in where there is a high geological background of PTMs, and by conducting a comparative with a larger-scale background dataset when calculating is the better way to solve the problem.

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Table and Figure Captions

Table 1 Brief description of sampled rocks and their underlying geological formations in the Baoshan area.

Table 2 Brief description of soils sampled in the Baoshan area.

Table 3 Analytical methods and detection limits.

Table 4 Average concentrations of major (wt.%) and trace elements ($\mu\text{g/g}$) for geological formations in the Baoshan area.

Table 5 Variance explained by each principal component and component loadings for PC1-PC4 of rock/ore samples.

Table 6 Average concentrations of major (wt.%) and trace elements ($\mu\text{g/g}$) for soils developed on different geological formations in the Baoshan area.

Table 7 Variance explained by each principal component and component loadings for PC1-PC6 of soil samples.

Table 8 Level of enrichment/depletion of chemical elements from the Baoshan soils from the different geological formations, relatively to the respective rocks, determined by Median soil content/Median underlying rock content.

Table 9 Numbers of contaminated soil samples from different geological formations in the Baoshan area.

Table 10 Average concentrations of extractable As, Cd and Pb ($\mu\text{g/g}$), and their percentage to total content in the soils developed on different geological formations in the Baoshan.

Fig. 1 Contour maps of altitude, average surface soil (0cm) temperature and annual rainfall for

study area.

Fig. 2 Simplified land-use (a) and soil-type (b) maps of study area.

Fig. 3 Simplified tectonic map of Yunnan Sanjiang area.

Fig. 4 Simplified geological and mineral deposits map of study area.

Fig. 5 Sample locations in each geological formation and near the HTP and HYA mining areas in this study.

Fig. 6 Biplots of the principal components for the clr-transformed whole composition of rock and ore samples, with parallel plots for grouping of rock/ ore samples by different geological formations in the PC1-PC2 (a) and PC1-PC3 (b) principal component space.

Fig. 7 Biplots of the principal components for the clr-transformed whole composition of soil samples, with parallel plots for grouping of soil samples by overlying different geological formations in the PC1-PC2 (a) and PC2-PC3 (b) principal component space.

Fig. 8 Median values of elements ratio (soil/rock) derived from the different geological formations to reflect the PTMs enrichment and depletion in soils related to their bedrocks.

Table 1 Brief description of sampled rocks and their underlying geological formations in the Baoshan area.

No	Sample Name	Formation Name	Sampled geological formation and deposit description*	Age/formation	Outcrop locations	Sampled rock (number)
1	C-1-R	C-1	Baoshan formation: Gray, yellow-green shale, sandstone containing limestone, argillaceous limestone; The lower section of Liushui formation: Yellow-green, grayish yellow siltstone, mudstone with argillaceous limestone	C_3b ; C_3l^I	The northernmost part of the middle line in the study area	Mudstone (9); limestone (1)
2	C-2-R	C-2	Upper section of Shahechang formation: shale and siltstone; Hetaoping formation: grayish green slate; The upper section of the Shuangmai formation: dark green rhythmic slate	C_{35}^2 ; C_3h ; C_{1-3sh}^3	North Central of the study area and northwest of Baoshan city	Mudstone (9); phyllite (2)
3	C-3-R	C-3	The upper section of Baoshan formation: shale, limestone with sandstone	C_3b^2	Central part of the study area	Limestone (8); siliceous limestone (2)
4	O-R	O	Mantang formation: grayish white sandstone, shale (slate)	O_1m	Central north and south part of the study area	Sandstone (2); mudstone (4); quartz sandstone (4)
5	S-R	S	Upper Renheqiao formation: light gray reticulated limestone; Lower Renheqiao formation: Black graptolite shale	S_{1r} ; S_{2r}	Distributed in the middle as narrow strip of the study area	Shale (7); limestone (3)
6	D-R	D	Shabajiao formation, Wangjiacun formation and Xiangyangsi formation are combined or not divided: sandy dolomite, argillaceous limestone, sandy limestone; Heyuanzhai formation: argillaceous limestone, pimple limestone; Dazhaimen formation: argillaceous limestone and calcareous mudstone	D_1 ; D_2hy ; D_3d	Widely distributed in the central south and northwest	Limestone (9); dolomite (1); siltstone (1)
7	C-R	C	Pumenqian formation and Xiangshan formation are combined or not divided: Oolitic limestone, chert limestone, mud limestone with argillaceous limestone in its lower part; Dingjiazhai formation: gray mudstone with argillaceous limestone, sandstone and conglomerate	C_1 ; C_3d	Midwest and northwest	Limestone (8); siliceous limestone (1); mudstone (1)
8	T-1-R	T-1-	The upper section of Dashuitang formation: limestone, chert limestone	T_3d^2	Widely distributed in the west and east part of the study area	Limestone (8); dolomitic limestone (1); dolomite (1)
9	T-2R	T-2	Hewanjie formation: dolomite	T_2h	Widely distributed in the west and east part of the study area	Dolomite (10)
10	J-R	J	Liuwan formation: limestone, shale and shell limestone	J_2l	Distributed in the west of the study area as long strips	Limestone (7); siliceous limestone (1); sandstone (2)
11	Ba-1-R	Ba-1	Woniusi formation: dense and amygdaloid basalt with limestone lens	C_3w	Northwest and northeast of the study area	Basalt (10)
12	Ba-2-R	Ba-2	The upper section of Mengjia formation: Basalt	J_2m^2	Southwest of the study area	Basalt (10)
13	HTP-O	HTP	Hetaoping Cu-Pb-Zn deposit. Main ore minerals: Galena, Chalcopyrite, Sphalerite, Pyrite, Pyrrhotite.	HTP	The northernmost part of study area	(Galena) (Chalcopyrite) Sphalerite (10)
14	HYA-O	HYA	Heiyanao Fe-Cu-Pb-Zn deposit. Main ore minerals: Pyrite, Chalcopyrite, Pyrrhotite, Magnetite, Hematite, Galena, Sphalerite.	HYA	The northernmost part of study area	(Galena) (Chalcopyrite) Sphalerite (5); chalcopyrite (1); pyrite (1); magnetite (3)

Table 2 Brief description of soils sampled in the Baoshan area.

No.	Sample Name	Soil type and soil characteristic description	Average height	Land use of sampled soils (number)	Under formation
1	C-1-S	Yellow brown soils/ dark yellow brown soils. Black brown, brown and earthy yellow fine grain loam.	2470 m	Forest land (10)	C-1
2	C-2-S	Brown/yellow brown soils. Brown, earthy yellow fine grain loam.	2672 m	Forest land (11)	C-2
3	C-3-S	Yellow-red soils/ Acid purple soils. Red, earthy yellow, fine-medium grain loam.	1989 m	Forest land (3); Shrubland (7)	C-3
4	O-S	Red soils/ dry red soils/ yellow red soils. Brown, earthy yellow fine-medium grain loam.	1473 m	Cultivated land/Dry land (6); Shrubland (4)	O
5	S-S	Yellow red soils/ red soils. Earthy yellow, red and brown fine-medium grain loam.	1876 m	Cultivated land/Dry land (6); Shrubland (4)	S
6	D-S	Yellow red soils/ red soils/ acid purple soils. Earthy yellow and brown fine-medium grain loam.	1981 m	Cultivated land/Dry land (7); Shrubland (4)	D
7	C-S	Red soils. Brown, yellow brown, brick-red and earthy yellow fine grain loam.	2205 m	Cultivated land/Dry land (4); Shrubland (6)	C
8	T-1-S	Red soils. Brown, brick-red and earthy yellow fine-coarse grain loam.	2018 m	Cultivated land/Dry land (7); Shrubland (3)	T-1
9	T-2-S	Red soils. Red and brown fine-medium grain loam.	1835 m	Cultivated land/Dry land (7); Shrubland (3)	T-2
10	J-S	Phaeozems/ red soils. Earthy yellow fine- medium grain loam.	861 m	Cultivated land/Dry land (2); Shrubland (8)	J
11	Ba-1-S	Red soils. Brown fine grain loam.	1708 m	Cultivated land/Dry land (4); Shrubland (6)	Ba-1
12	Ba-2-S	Phaeozems/ red soils. Brown fine grain loam. The thickness of soil is extremely thin.	958 m	Wasteland (4); Shrubland (6)	Ba-2
13	HTP-S	Red soils. Brown fine grain loam.	2151 m	Forest land (10)	HTP
14	HYA-S	Yellow brown soils. Brown fine grain loam.	1966 m	Shrubland (10)	HYA

Table 3 Analytical methods, devices, and detection limits.

Indicator	Analytical method	Brand and the model of analysis device	Detection limit	Unit	Sample
Al ₂ O ₃	XRF	Shimadzu; XRF-1800X	0.03	wt. %	Rock and soil
CaO	XRF	Shimadzu; XRF-1800X	0.02	wt. %	Rock and soil
TFe ₂ O ₃	XRF	Shimadzu; XRF-1800X	0.02	wt. %	Rock and soil
K ₂ O	XRF	Shimadzu; XRF-1800X	0.03	wt. %	Rock and soil
Na ₂ O	XRF	Shimadzu; XRF-1800X	0.02	wt. %	Rock and soil
MgO	XRF	Shimadzu; XRF-1800X	0.02	wt. %	Rock and soil
SiO ₂	XRF	Shimadzu; XRF-1800X	0.05	wt. %	Rock and soil
As	AFS	Jitian; AFS-820	0.2	µg/g	Rock and soil
Ba	ICP-OES	ThermoFisher; ICAP6300	5	µg/g	Rock and soil
Cd	ICP-MS	ThermoFisher; X2	0.02	µg/g	Rock and soil
Cr	ICP-OES	ThermoFisher; ICAP6300	1.5	µg/g	Rock and soil
Cs	ICP-MS	ThermoFisher; X2	0.2	µg/g	Rock and soil
Cu	ICP-MS	ThermoFisher; X2	0.1	µg/g	Rock and soil
Hf	XRF	Shimadzu; XRF-1800X	0.1	µg/g	Rock and soil
Hg	AFS	Jitian; AFS-820	0.0005	µg/g	Rock and soil
Nb	ICP-MS	ThermoFisher; X2	1.4	µg/g	Rock and soil
Ni	ICP-OES	ThermoFisher; ICAP6300	0.2	µg/g	Rock and soil
Pb	ICP-MS	ThermoFisher; X2	0.2	µg/g	Rock and soil
Rb	ICP-MS	ThermoFisher; X2	0.1	µg/g	Rock and soil
S	HFIR	Saiensi; HCS-801A	15	µg/g	Rock and soil
Sr	ICP-OES	ThermoFisher; ICAP6300	2	µg/g	Rock and soil
Ta	ICP-MS	ThermoFisher; X2	0.1	µg/g	Rock and soil
Th	ICP-MS	ThermoFisher; X2	0.2	µg/g	Rock and soil
U	ICP-MS	ThermoFisher; X2	0.02	µg/g	Rock and soil
Zn	ICP-MS	ThermoFisher; X2	1	µg/g	Rock and soil
Zr	XRF	Shimadzu; XRF-1800X	1.5	µg/g	Rock and soil
C.org	VOL	-	0.02	µg/g	Soil
pH	ISE	Leici; PHS-3C	0.01	-	Soil
Extractable As	AFS	Jitian; AFS-820	0.01	µg/g	Soil
Extractable Cd	ICP-MS	ThermoFisher; X2	0.001	µg/g	Soil
Extractable Pb	ICP-MS	ThermoFisher; X2	0.004	µg/g	Soil

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Notation: XRF: X-Ray Fluorescence Spectrometry; AFS: Cold Vapor-Atomic Fluorescence Spectrometry; ICP-MS: Inductively

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Coupled Plasma-Mass Spectrometry; ICP-OES: Inductively Coupled Plasma-Optical Emission Spectroscopy; HFIR: High frequency

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combustion infrared absorption; VOL: volumetric; ISE: Ion Selective Electrode; wt. %: Weight percent

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Table 4 Average concentrations of major (wt.%) and trace elements ($\mu\text{g/g}$) for geological formations in the Baoshan area.

	UCC	€-1-R	€-2-R	€-3-R	O-R	S-R	D-R	C-R	T-1-R	T-2-R	J-R	HTP-O	HYA-O	Ba-1-R	Ba-2-R
	Median	Median	Median	Median	Median	Median	Median	Median	Median	Median	Median	Median	Median	Median	Median
Al ₂ O ₃	15.40	20.94	21.56	0.51	14.00	14.04	1.31	0.96	0.05	0.11	1.91	2.45	0.52	14.63	14.28
CaO	3.59	0.06	0.06	54.72	0.05	0.29	51.68	46.87	55.34	30.84	46.14	12.39	10.78	7.51	8.43
TFe ₂ O ₃	5.04	7.87	9.25	0.34	3.70	4.62	0.57	0.45	0.04	0.21	1.54	17.79	30.01	12.42	13.36
K ₂ O	2.80	5.05	4.12	0.08	2.32	3.98	0.34	0.14	0.01	0.01	0.29	0.43	0.17	0.73	0.53
Na ₂ O	3.27	0.13	0.15	0.07	0.16	0.16	0.09	0.07	0.08	0.11	0.11	0.09	0.11	2.73	2.62
MgO	2.48	3.34	3.92	0.27	0.69	1.12	0.71	0.84	0.62	21.77	1.40	1.88	2.59	5.77	6.28
SiO ₂	66.60	55.44	53.59	0.68	71.38	63.84	3.61	12.23	0.24	0.26	7.80	26.93	29.45	49.77	46.24
As	4.80	12.74	4.50	2.11	6.53	0.99	1.61	4.79	0.62	1.37	2.11	134.60	143.31	1.08	0.99
Ba	628.00	608.09	762.87	44.81	613.67	595.02	50.20	46.72	29.35	30.50	58.63	137.00	40.51	246.83	150.08
Cd	0.09	0.05	0.09	0.05	0.03	0.05	0.05	0.12	0.16	0.07	0.06	125.03	14.23	0.22	0.05
Cr	92.00	140.05	150.27	4.93	75.91	66.43	7.71	11.56	5.82	6.11	10.13	17.51	9.00	136.06	298.44
Cs	4.90	10.34	7.31	0.77	4.63	7.72	1.55	0.56	0.23	0.20	1.03	14.06	8.53	0.32	0.27
Cu	28.00	43.10	52.98	2.48	19.60	24.12	3.01	3.25	1.49	2.57	6.90	5500	571.24	124.68	61.65
Hf	5.30	2.45	2.60	0.55	6.60	5.65	0.90	1.00	0.65	0.40	0.70	4.35	0.85	3.15	2.95
Hg	0.05	0.02	0.01	0.12	0.02	0.01	0.01	0.05	0.03	0.07	0.02	0.76	0.18	0.03	0.01
Nb	12.00	16.15	15.81	0.59	13.18	12.43	2.48	1.70	0.44	0.28	1.59	1.46	0.63	9.97	8.89
Ni	47.00	61.54	69.33	1.95	21.13	33.43	3.97	4.17	1.99	1.48	7.78	8.61	2.86	67.99	271.45
Pb	17.00	10.54	12.20	7.18	10.00	9.39	3.39	3.09	2.41	4.27	10.96	54500	223.21	17.62	7.47
Rb	84.00	237.42	190.80	11.49	109.62	173.66	17.22	10.70	2.04	2.20	10.15	26.35	5.94	16.02	8.28
S	621.00	44.09	48.71	62.55	48.71	67.17	307.14	138.70	79.20	120.65	288.74	93500	13600	112.01	55.42
Sr	320.00	14.93	34.62	242.35	25.04	57.26	275.58	398.03	72.38	43.89	246.53	86.44	34.92	198.48	193.60
Ta	0.90	1.74	1.69	0.11	1.44	1.24	0.21	0.17	0.09	0.06	0.19	0.27	0.13	0.92	0.78
Th	10.50	22.27	21.94	2.73	18.18	18.32	2.99	3.75	0.53	0.96	1.60	2.49	0.91	2.98	2.32
U	2.70	2.34	2.75	0.57	2.73	2.49	0.60	0.66	0.86	0.83	0.84	0.68	0.49	0.51	0.44
Zn	67.00	99.32	118.62	11.93	40.58	41.78	18.68	15.15	6.18	13.93	27.63	63490	7856.30	136.49	107.73
Zr	193.00	99.05	98.10	7.95	216.50	198.60	20.70	17.20	5.50	4.20	17.00	103	4.90	110.70	103.65

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UCC: upper continental crust (Rudnick and Gao, 2003).

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737 **Table 5 Variance explained by each principal component and component**
738 **loadings for PC1-PC4 of rock/ore samples.**

	PC1	PC2	PC3	PC4
Percentage of Variance	46.9%	19.1%	11.7%	4.5%
Cumulative Percent	46.9%	66.0%	77.7%	82.2%
	PC1	PC2	PC3	PC4
Al ₂ O ₃	-0.24	-0.18	-0.08	0.11
CaO	0.12	0.37	-0.07	0.17
TFe ₂ O ₃	0.01	-0.35	-0.24	-0.12
K ₂ O	-0.21	-0.23	0.14	0.02
Na ₂ O	-0.12	0.19	-0.37	-0.09
MgO	-0.01	0.27	-0.17	-0.57
SiO ₂	-0.13	-0.30	-0.12	0.25
As	0.21	-0.06	0.18	-0.09
Ba	-0.21	-0.05	0.18	-0.25
Cd	0.27	-0.04	0.01	0.01
Cr	-0.23	0.01	-0.22	-0.20
Cs	0.02	-0.18	0.45	-0.15
Cu	0.16	-0.28	-0.17	-0.10
Hf	-0.18	0.13	0.02	0.35
Hg	0.21	0.20	0.15	-0.00
Nb	-0.28	-0.02	-0.02	0.07
Ni	-0.22	-0.03	-0.28	-0.15
Pb	0.23	-0.13	0.03	0.12
Rb	-0.21	-0.08	0.35	-0.07
S	0.27	0.01	0.06	0.09
Sr	0.01	0.37	-0.05	0.30
Ta	-0.27	0.05	0.03	-0.03
Th	-0.23	0.05	0.26	-0.02
U	-0.12	0.25	0.29	-0.20
Zn	0.23	-0.23	-0.08	-0.06
Zr	-0.24	-0.02	-0.01	0.30

739 **Table 6 Average concentrations of major (wt.%) and trace elements (µg/g) for soils developed on different geological formations in**
740 **the Baoshan area.**

	Deep soil of CGB	BL	Є-1-S	Є-2-S	Є-3-S	O-S	S-S	D-S	C-S	T-1-S	T-2-S	J-S	HTP-S	HYA-S	Ba-1-S	Ba-2-S
	Median	Median	Median	Median	Median	Median	Median	Median	Median	Median	Median	Median	Median	Median	Median	Median
Al ₂ O ₃	11.9	18.29	19.88	18.87	23.36	17.25	18.70	18.01	16.06	25.38	20.20	15.31	18.11	18.57	14.38	16.15
CaO	2.57	0.62	0.24	0.16	0.29	0.09	0.26	0.50	0.37	0.62	3.63	10.02	2.04	0.59	4.35	6.30
TFe ₂ O ₃	4.1	8.05	7.93	8.84	9.34	5.25	5.92	7.58	7.21	10.18	13.15	6.03	8.19	7.21	12.72	9.97
K ₂ O	2.36	2.56	2.77	2.06	2.70	2.78	3.58	3.38	0.91	1.36	1.27	2.31	1.91	3.13	0.65	1.44
Na ₂ O	1.81	0.17	0.15	0.16	0.13	0.16	0.11	0.11	0.10	0.12	0.10	0.26	0.25	0.15	1.36	0.29
MgO	1.36	1.28	1.27	1.24	0.78	0.54	1.19	1.20	0.65	1.07	3.16	1.96	2.48	2.17	4.47	2.33
SiO ₂	67.9	59.68	50.16	49.06	49.90	66.27	61.32	57.79	61.47	44.74	39.79	47.80	45.92	53.28	44.78	46.40
As	9	18.73	17.16	10.02	30.72	7.57	8.26	14.08	28.42	28.58	26.00	12.05	196.19	166.62	1.27	6.17
Ba	522	341.60	382.65	435.26	305.27	538.13	467.65	319.19	167.63	257.18	163.96	248.37	599.92	855.50	158.38	258.31
Cd	0.11	0.13	0.21	0.21	0.22	0.10	0.11	0.15	0.37	3.61	0.57	0.16	4.51	7.44	0.11	0.14
Cr	50	119.00	111.93	115.50	133.40	94.26	98.89	119.46	116.75	164.16	190.05	92.63	113.42	112.31	196.85	184.53
Cs	6	-	14.00	9.36	21.24	6.19	11.14	16.46	7.10	16.99	12.12	8.54	15.24	13.03	1.19	5.50
Cu	19	45.19	43.86	41.12	64.07	28.46	28.84	30.08	47.96	63.17	71.86	30.42	162.39	623.57	124.71	49.51
Hf	6.1	-	3.90	3.70	6.60	8.25	7.25	8.50	5.20	6.95	4.30	3.85	4.10	7.40	2.70	3.70
Hg	0.018	0.11	0.20	0.23	0.58	0.05	0.06	0.06	0.20	0.27	0.51	0.03	0.34	0.40	0.02	0.02
Nb	12	20.19	17.28	19.72	24.06	18.26	20.73	35.45	26.69	26.89	26.89	14.19	15.79	21.20	11.79	15.16
Ni	22	57.74	44.95	32.94	72.19	28.03	43.35	50.64	75.53	110.16	59.59	48.43	65.99	64.76	64.53	132.72
Pb	21	30.65	48.93	37.93	123.16	28.80	28.95	38.54	30.73	66.48	98.96	19.13	334.16	2318.46	8.06	14.98
Rb	96	137.20	161.72	109.49	166.22	133.95	185.02	187.96	63.84	94.33	59.43	111.60	156.01	179.96	26.00	58.81
S	166	127.01	469.25	462.79	199.83	142.21	152.50	226.58	190.23	304.23	181.90	127.43	764.20	332.54	98.64	177.28
Sr	197	63.00	31.14	31.33	34.55	23.33	50.31	63.30	214.25	42.43	76.18	103.28	53.73	37.17	149.74	70.68
Ta	1	-	1.19	1.41	1.65	1.25	1.51	2.44	1.95	2.23	1.99	1.04	1.17	1.57	0.75	1.21
Th	10	15.69	20.25	19.84	26.35	18.36	20.99	22.14	17.61	21.73	12.24	11.30	17.12	20.20	3.93	7.54
U	2.4	3.08	3.09	3.06	3.60	3.36	3.06	3.58	3.60	4.72	4.13	2.20	1.96	2.60	0.62	1.73
Zn	60	100.25	119.19	84.35	195.10	43.01	77.17	100.25	139.94	219.28	183.51	68.75	574.92	3236.94	101.43	87.86
Zr	215	232.15	134.94	148.20	246.71	252.80	246.86	260.37	179.24	277.65	204.73	150.18	148.30	193.35	117.66	139.49
C.org	0.3	0.59	6.73	7.07	1.80	1.70	1.39	1.97	1.53	1.96	1.38	1.16	4.73	1.80	1.03	1.74
pH	8.1	6.57	5.13	5.06	5.61	5.18	5.61	6.39	5.75	6.66	7.99	8.36	7.33	6.80	6.91	8.19

741 Deep soil of CGB: the deep soil from China geochemical baseline project (CGB; [Wang et al., 2016](#))

742 BL: background level, median value of deep soil from the 1:250000 scale land quality geochemical of study area.

743 **Table 7 Variance explained by each principal component and component**
744 **loadings for PC1-PC6 of soil samples.**

	PC1	PC2	PC3	PC4	PC5	PC6
Percentage of Variance	33.3%	27.2%	9.0%	8.0%	6.3%	3.9%
Cumulative Percent	33.3%	60.5%	69.5%	77.6%	83.9%	87.8%
	PC1	PC2	PC3	PC4	PC5	PC6
Al ₂ O ₃	-0.28	-0.08	0.02	0.03	-0.13	0.21
CaO	0.07	-0.27	-0.03	0.21	0.38	-0.04
TFe ₂ O ₃	-0.14	-0.25	0.06	0.05	-0.30	0.21
K ₂ O	-0.18	0.19	-0.22	-0.11	0.29	0.29
Na ₂ O	-0.09	-0.28	-0.26	-0.12	-0.03	-0.02
MgO	0.01	-0.29	-0.17	0.06	0.12	0.07
SiO ₂	-0.28	-0.04	-0.11	-0.15	-0.04	-0.16
As	0.21	0.21	0.14	0.06	0.00	-0.05
Ba	-0.09	0.13	-0.41	-0.34	0.00	0.06
Cd	0.28	0.05	0.11	-0.03	-0.03	-0.12
Cr	-0.17	-0.25	0.09	-0.01	-0.20	0.29
Cs	-0.04	0.27	0.14	0.19	0.20	0.35
Cu	0.20	-0.13	-0.03	-0.35	-0.22	0.06
Hf	-0.25	0.09	0.05	-0.25	0.05	-0.34
Hg	0.14	0.17	0.27	0.16	-0.26	0.07
Nb	-0.28	0.04	0.23	-0.02	-0.08	-0.14
Ni	-0.07	-0.26	0.23	-0.02	-0.08	0.34
Pb	0.24	0.19	0.03	-0.22	-0.05	0.00
Rb	-0.14	0.26	-0.16	-0.06	0.26	0.24
S	0.04	0.10	-0.35	0.41	-0.23	-0.13
Sr	-0.09	-0.25	0.07	0.10	0.17	-0.41
Ta	-0.26	0.05	0.26	0.06	-0.06	-0.09
Th	-0.20	0.27	0.04	0.01	-0.02	0.06
U	-0.20	0.20	0.18	0.15	0.03	-0.11
Zn	0.28	0.02	0.06	-0.29	-0.09	-0.02
Zr	-0.28	0.03	0.12	-0.18	0.01	-0.19
C. org	-0.05	0.09	-0.37	0.39	-0.27	-0.10
pH	0.12	-0.20	0.12	0.11	0.44	0.02

Table 8 Level of enrichment/depletion of chemical elements from the Baoshan soils from the different geological formations, relatively to the respective rocks, determined by Median soil content/Median underlying rock content.

	€-1	€-2	€-3	O	S	D	C	T-1	T-2	J	HTP	HYA	Ba-1	Ba-2
Al ₂ O ₃	0.94	0.86	48.05	1.21	1.18	14.58	16.23	396.76	161.01	6.77	6.91	34.69	0.99	1.12
CaO	6.15	2.58	0.01	1.64	0.48	0.01	0.01	0.01	0.12	0.32	0.16	0.05	0.51	0.87
TFe ₂ O ₃	1.05	0.98	25.90	1.13	1.24	11.18	16.61	306.65	60.63	4.08	0.49	0.24	1.09	0.73
K ₂ O	0.56	0.57	29.39	1.09	0.79	9.80	15.35	118.93	102.36	8.95	4.87	18.25	0.79	3.05
Na ₂ O	1.09	1.13	1.93	0.70	0.79	1.16	1.34	1.51	0.85	2.34	2.23	1.48	0.54	0.09
MgO	0.42	0.33	3.05	0.78	0.91	1.76	1.78	1.72	0.14	1.16	1.35	0.94	0.83	0.37
SiO ₂	0.90	0.95	72.63	0.91	0.99	15.31	4.77	163.20	133.12	5.35	1.48	1.83	0.90	0.93
As	3.19	5.90	14.71	1.98	6.56	8.87	7.95	40.98	24.23	6.14	1.97	1.07	1.13	5.98
Ba	0.61	0.62	7.35	1.03	0.86	6.37	3.06	9.31	5.61	3.38	3.73	20.59	0.89	1.22
Cd	5.47	1.86	6.56	2.99	2.69	2.61	3.70	22.27	8.65	2.80	0.04	0.55	0.49	2.54
Cr	0.78	0.80	25.78	1.19	1.52	13.00	11.04	26.27	28.90	7.28	6.04	12.95	1.28	0.62
Cs	1.40	1.13	25.99	1.67	1.49	15.16	11.21	64.99	61.07	10.80	0.74	1.69	2.71	22.21
Cu	0.98	0.78	24.59	1.20	2.07	10.99	12.09	39.65	25.79	3.66	0.05	1.23	1.13	0.64
Hf	1.59	1.40	11.57	1.27	1.45	9.33	4.84	11.75	12.03	4.29	2.27	9.23	0.94	1.45
Hg	14.63	21.24	4.69	2.01	3.24	4.15	3.32	15.23	4.63	2.16	0.38	1.98	0.80	2.59
Nb	1.08	1.24	39.54	1.58	1.48	13.90	13.61	58.53	73.93	8.80	9.29	33.10	1.23	1.73
Ni	0.80	0.52	36.15	1.08	1.01	11.49	18.86	61.39	47.20	5.24	7.15	22.75	0.96	0.68
Pb	5.84	4.30	19.01	2.89	2.42	8.91	10.09	23.41	23.26	1.75	0.02	13.72	0.53	1.55
Rb	0.74	0.60	13.92	1.20	0.97	11.39	5.03	47.64	32.86	13.74	5.31	28.58	1.93	9.13
S	9.77	8.52	3.21	2.67	2.05	0.67	1.18	3.35	1.74	0.68	0.01	0.03	0.90	2.93
Sr	2.15	0.77	0.15	0.88	0.77	0.29	0.45	0.62	1.89	0.42	0.79	1.05	0.71	0.39
Ta	0.77	0.81	15.46	1.08	1.16	10.92	9.25	25.09	26.90	5.94	4.23	11.94	0.82	1.48
Th	0.90	0.91	10.07	1.05	1.01	6.97	4.40	34.44	13.61	7.21	7.01	24.29	1.32	3.22
U	1.44	1.19	6.96	1.12	1.28	6.22	5.38	6.54	6.18	2.79	3.23	5.52	1.45	3.78
Zn	1.15	0.69	16.85	1.01	1.59	4.92	6.99	36.24	13.19	2.98	0.01	0.42	0.67	0.76
Zr	1.39	1.42	29.27	1.19	1.13	12.44	10.12	43.31	46.01	6.37	1.62	38.14	1.07	1.49

Table 9 Numbers of contaminated soil samples from different geological formations in the Baoshan area.

PTMs	Methods	Numbers of soil samples														Total
		C-1	C-2	C-3	O	S	D	C-1	T-1	T-2	J	HTP	HYA	Ba-1	Ba-2	
As	Igeo	Bn=BL	1	1	-	-	-	1	-	-	-	9	10	-	-	22
		Bn=CGB	2	1	1	-	-	4	-	2	-	10	10	-	-	30
		EF	6	7	-	3	7	1	-	-	2	1	-	3	10	40
		>RSV	4	3	6	-	-	6	6	5	-	10	10	-	-	50
Cd	Igeo	Bn=BL	2	-	-	-	-	2	10	3	-	9	10	-	-	36
		Bn=CGB	-	-	-	-	-	5	10	4	-	10	10	-	-	39
		EF	6	6	-	-	-	-	-	-	1	-	-	-	5	18
		>RSV	3	1	3	1	1	6	10	6	-	10	10	-	-	51
Cr	Igeo	Bn=BL	-	-	-	-	-	-	-	-	-	-	-	-	-	0
		Bn=CGB	-	-	-	-	-	1	-	-	-	-	-	3	2	6
		EF	-	-	-	-	1	-	-	-	-	-	-	-	3	4
		>RSV	-	1	1	-	1	1	4	3	-	-	-	5	4	17
Cu	Igeo	Bn=BL	-	-	-	-	-	-	-	-	-	-	-	-	-	0
		Bn=CGB	-	-	-	-	-	1	-	2	-	9	10	6	-	28
		EF	-	-	-	1	3	2	-	-	1	-	-	1	-	8
		>RSV	3	3	7	-	-	3	4	2	-	9	10	8	-	49
Hg	Igeo	Bn=BL	-	-	4	-	-	1	-	5	-	2	-	-	-	12
		Bn=CGB	10	10	11	-	2	7	10	8	1	10	10	-	-	79
		EF	10	10	-	4	6	1	-	-	3	-	-	2	5	41
		>RSV	-	-	1	-	-	1	-	-	-	-	-	-	-	2
Ni	Igeo	Bn=BL	-	-	-	-	-	-	-	-	-	-	-	-	-	0
		Bn=CGB	-	-	-	-	-	-	1	2	-	-	-	3	5	11
		EF	-	-	-	-	2	-	-	-	-	2	1	1	-	6
		>RSV	3	1	6	-	1	-	-	3	-	9	10	-	-	49
Pb	Igeo	Bn=BL	-	-	2	-	-	-	-	2	-	7	10	-	-	21
		Bn=CGB	-	1	4	-	-	-	-	3	-	9	10	-	-	27
		EF	10	10	-	5	4	2	-	-	-	-	1	-	4	36
		>RSV	1	2	9	-	1	-	-	3	-	9	10	-	-	35
Zn	Igeo	Bn=BL	-	-	-	-	-	-	-	-	-	4	10	-	-	14
		Bn=CGB	-	-	-	-	-	-	1	2	-	7	10	-	-	20
		EF	-	-	-	1	2	-	-	-	-	-	-	-	-	3
		>RSV	1	3	1	-	-	-	7	3	-	9	10	-	-	34

BL: background level, median value of deep soil from the 1:250000 scale land quality geochemical of study area.

CGB: the median value of deep soil of China geochemical Baseline project (Wang et al., 2016).

RSV: the risk screening values for soil contamination of agricultural land of the People's Republic of China

(Ministry of Ecology and Environment of The People's Republic of China, 2018).

Soils with the PTMs Igeo index or EF value >2 are thought to be contaminated in this study.

Table 10 Average concentrations of extractable As, Cd and Pb (µg/g), and their percentage to total content in the soils developed on different geological formations in the Baoshan.

	Extractable Cd	Ex Cd Ratio	Extractable Pb	Ex Pb Ratio	Extractable As	Ex As Ratio
	Median	Median	Median	Median	Median	Median
C-1	0.022	0.116	0.039	0.001	-	-
C-2	0.022	0.127	0.074	0.002	-	-
C-3	0.022	0.097	0.104	0.001	-	-
O	0.019	0.198	0.049	0.002	-	-
S	0.014	0.161	0.113	0.004	-	-
D	0.016	0.127	0.137	0.005	-	-
C	0.024	0.087	0.144	0.022	-	-
T-1	0.250	0.068	3.012	0.043	-	-
T-2	0.103	0.158	6.773	0.071	-	-
J	0.015	0.086	0.879	0.051	-	-
HTP	0.794	0.119	17.511	0.052	-	-
HYA	1.657	0.222	631.620	0.289	0.001226248	0.00001
Ba-1	0.013	0.120	0.140	0.020	-	-
Ba-2	0.009	0.084	0.416	0.030	-	-

Ex Cd Ratio: Extractable ratio of Cd, calculated by $(Cd_{\text{extractable}}) / (Cd_{\text{total content}})$, same to Pb and As.

Fig. 1 Simplified tectonic map of Yunnan Sanjiang area (After Wang et al., 2010; Li et al., 2015).

Fig. 2 Contour maps of altitude, average surface soil (0cm) temperature and annual rainfall for study area.

(Altitude data, surface soil temperature data and rainfall data from National Earth System Science Data Sharing Infrastructure, National Science & Technology Infrastructure of China. (<http://www.geodata.cn>))

Fig. 3 Simplified land-use (a) and soil-type (b) maps of study area.

YBS: yellow brown soils; DYBS: dark yellow brown soils; BS: brown soils; DRS: dry red soils; EDRS: eluvial dry laterite; CRS: cinnamon red soils; RLS: red lime soils; LS: lime soils; APS: acid purple soils; PS: paddy soils; PRS: permeate rice soils; DFS: dark felty soils; YCRS: yellow crimson red soils; RS: red soils; YRS: yellow red soils; MRS: mountain red soils; RYS: rinse yellow soils; ReS: reservoir soils.

Fig. 4 Simplified geological and mineral deposits map of study area.

(Geological map simplified from Yunnan geological and mineral development bureau regional geological survey team, 1981,1983,1986; Mineralization map from CGS mineral resources database <http://geocloud.cgs.gov.cn>)

O: mineralized spot/occurrence; S small-sized deposit; M; medium-sized deposit; L: large to super large sized deposit

Fig. 5 Sample locations in each geological formation and near the HTP and HYA mining areas in this study. Deposits also showed in this map.

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777 **Fig. 6 Biplots of the principal components for the clr-transformed whole**
778 **composition of rock and ore samples, with parallel plots for grouping of rock/**
779 **ore samples by different geological formations in the PC1-PC2 (a) and PC1-PC3**
780 **(b) principal component space.**

781

Fig. 7 Biplots of the principal components for the clr-transformed whole composition of soil samples, with parallel plots for grouping of soil samples by overlying different geological formations in the PC1-PC2 (a) and PC2-PC3 (b) principal component space.

788 **Fig. 8 Median values of elements ratio (soil/rock) in derived from the different**
789 **geological formations to reflect the PTMs enrichment and depletion in soils**
790 **related to their bedrocks.**