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Contamination, oral bioaccessibility and human health risk assessment of thallium and other metal(loid)s in farmland soils around a historic Tl—Hg mining area

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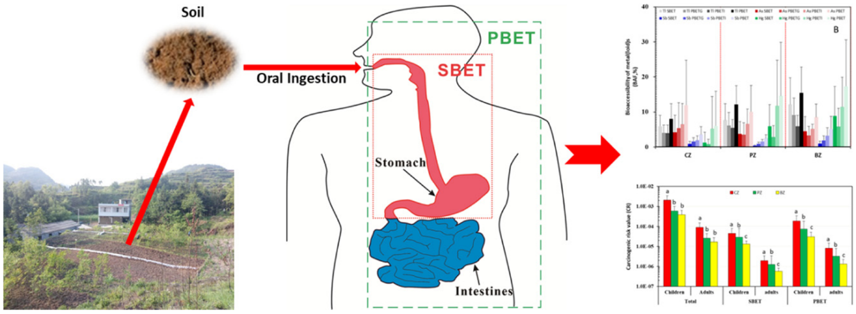
HIGHLIGHTS

- Elevated concentrations of Tl, Hg, As and Sb were determined in soils
- Bioaccessibility of Tl, Hg, As and Sb were relatively low and varied greatly among metal(loid)s and sampling sites.
- Bioaccessibility values of Tl, Hg, As and Sb by SBET were usually lower that those by PBET
- Health risk to children exceeded adults through oral ingestion
- Considering oral bioaccessibility was proposed as a more appropriate approach to assess human health risks of metal(loid)s.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, twenty-nine soil samples were collected from a historic Tl—Hg mining area, located in southwest Guizhou, China. Total concentrations of metal(loid)s in soils and *in vitro* extracts were analysed by ICP-MS, and the bioaccessibility of metal(loid)s was conducted by two often used *in vitro* extraction methods, Simplified bioaccessibility Extraction Test (SBET) and Physiologically Based Extraction Test (PBET). The health risk assessment based on total concentrations of metal(loid)s, bioaccessibility of SBET and PBET through soil ingestion were investigated. Results indicated that the collected cultivated soils contained elevated concentrations of Tl (44.8 ± 67.7 mg kg^{-1}), Hg (110 ± 193 mg kg^{-1}), As (84.4 ± 89.2 mg kg^{-1}) and Sb (14.8 ± 24.8 mg kg^{-1}), exceeding the regional background values of Guizhou province, China and the Chinese farmland risk screening values. However, the bioaccessibility of Tl, Hg, As and Sb were relatively low, usually less than 30% for most samples and varied greatly among metal(loid)s and sampling sites. The average bioaccessibility values of Tl, Hg, As and Sb by SBET were lower than those by PBET. The non-carsinogenic risk (HQ and HI) and Carcinogenic Risk (CR) values were significantly reduced when incorporating the bioaccessibiltiy of metal(loid)s into health risk assessment. It is worth noting that the health risk to children exceeded adults. Moreover, Tl and As contributed the most to the risk, indicating that more attention should be paid on Tl and As during the daily environmental regulation and management of contaminated soils in Lanmuchang.

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1. Introduction

Thallium (Tl), as a dispersed metal element, is widely distributed and usually occurs in trace concentrations in nature (Xiao et al., 2012; Jia et al., 2013). Thallium exhibits dual-geochemical character, with strong lithophile character like K and chalcophile character that makes it to be easily bound to S, and thus Tl is always found to be enriched in potassium feldspars and sulphides such as pyrite, marcasite and sphalerite (Xiao et al., 2004a, Xiao et al., 2012; Xiong, 2009; Martin et al., 2018; Liu et al., 2019; Vaněk et al., 2020). Thallium and its chemicals are very useful and often used in pharmaceutical, electronic, optical and superconducting materials industry (Zhou and Chen, 2008; Cvjetko et al., 2010; Liu et al., 2019). In past decades, large amounts of Tl have entered and enriched in soils caused by increasingly intense exploitation of minerals resource containing Tl (Xiao et al., 2003a, 2003b, 2004a, 2004b, 2012; Vaněk et al., 2013; Ning et al. 2015; Liu et al. 2019, 2020a; Lin et al. 2020; Rasool et al. 2020). However, Tl is considered as a typical non-essential and toxic element for human, and is classified as one of the 13 priority pollutant metals (Keith and Telliard, 1979; Xiao et al., 2012). Soil contamination by Tl has been an emerging and worldwide environmental concern, particularly in sulphide mining and smelting areas (Xiao et al., 2012; Liu et al. 2019).

Previous researches have reported that serious Tl contamination usually occurs in sulphide mining and smelting areas, and documented that Tl-polluted soils can potential threat to human health (Peter and Viraraghavan, 2005; Jakubowska et al. 2007; Karbowska et al., 2014; Xiao et al., 2012; Vanek et al. 2018; Liu et al. 2019, 2020a). Hand/object-to-mouth oral ingestion is a critical exposure pathway of hazardous materials for human (Paustenbach, 2000; Denys et al. 2012). Therefore, it is very vital to accurately assess potential human risk of Tl through soil ingestion. Traditional health risk assessment is usually assumed that total ingested potentially toxic elements are absolutely bioavailable. However, the health risks of potentially toxic elements for human by soil ingestion only depend on the fraction that is soluble in the gastrointestinal environment and available to be adsorbed by gastrointestinal tract (Ruby et al., 1999; Oomen et al. 2002; Luo et al. 2012; Denys et al. 2012; Li et al. 2014). In recent decades, many *in vivo* and *in vitro* bioaccessibility tests have been developed to predict the bioaccessibility of metal(loid)s in soils. Generally, *in vivo* animal models are deemed to be the optimal methods to determine the bioaccessibility of metal(loid)s in soils. However, these tests are time-consuming, costly, and involve ethical argument (Zia et al. 2011; Huang et al. 2018; Fernandez-Caliani et al. 2019; Cao et al. 2020). As an alternative, *in vitro* digestion models have been preferentially recommended and used to assess the bioaccessibility of metal(loid)s in a variety of contaminated soils, although such tests are only validated by *in vivo* tests for Pb, Cd and As at present (Juhasz et al. 2014; Li et al. 2014, 2015; Cao et al. 2020). The physiologically based extraction test (PBET) and the simplified bioaccessibility extraction test (SBET) are two most often-used methods to simulate the biochemical digestion process in the human gastrointestinal tract (Ruby et al., 1996; Luo et al. 2012; Li et al. 2014). PBET is essentially a two-stage sequential extraction using various enzymes to simulate both gastric and small intestine compartments (Ruby et al., 1996). SBET, as a simplified form of the PBET, is a one-step extraction to simulate gastric condition (Oomen et al. 2002; Li et al. 2014).

Lanmuchang, a rural area located in the southwest Guizhou of Southwest China, is a typical Tl-mineralized area, accompanied with Hg-As-Sb-Au mineralization, and has suffered sporadic exploitation of Tl since 1990s (Xiao et al. 2004a). Currently, the toxicity of Hg and As are well known while the understating on human health effects of Tl and Sb are relatively scarce. Both Tl and Sb are considered to be nonessential and toxic to humans. Antimony could cause diseases to liver, skin, and respiratory and cardiovascular systems (Schnorr et al. 1995; Li et al. 2014), and Tl poisoning could induce a series of symptoms like gastroenteritis, polyneuropathy, alopecia and even death may occur when people expose to high Tl concentration (Smith and Carson 1977; Chen and Liu, 1985; Mulkey and Oehme, 1993; Xiao et al., 2004a, 2004b, 2012; Liu et al. 2016, 2020b). Previous studies have suggested that local soils are severely polluted and highly enrich Tl and other metal(loid)s such as Hg, As and Sb (Xiao et al. 2004b, 2012; Lin et al. 2020). And Tl in local contaminated soils can be readily up-taken and accumulated in local vegetables such as green cabbage, and even be transferred into human body through the food chain, posing a significant health risk to local residents (Xiao et al. 2004b, 2007, 2012; Jia et al. 2013; Ning et al. 2015). Besides, a comprehensive health risk assessment based on total concentrations of Tl, Hg, As, and Sb in Lanmuchang area has been recently investigated by our research group (Ma et al. 2020). Yet, the human health risk assessment considering the bioaccessibility of Tl and other metal(loid)s through oral ingestion in local soils has not been studied. The main objectives of this study are: (1) to investigate the human bioaccessibility of Tl, Hg, As and Sb using PBET and SBET models in soils of Lanmuchang area, and (2) then to estimate potential non-carcinogenic and carcinogenic human health risks of Tl, Hg, As and Sb through soil ingestion. 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 Lanmuchang area (105°29′E-105°31′E, 25°29′N-25°32′N), located in southwest Guizhou province, China, is a typical farming area, and presently is mainly developed for agricultural and residential purpose. But it has a long mining and smelting history for mercury, and has been exploited for Tl since 1990s due to the existence of independent thallium deposits and large mineralization area of Tl-Hg-As-Au (Xiao et al. 2004a). The comprehensive information on mineralogy, petrology and geochemistry of this mineralization area was given in our previous works (Xiao et al., 2000, 2003a, 2003b, 2004a, 2004b, 2007). According to the geological characters and anthropogenic activities, the study area can be divided into three zones, core zone (CZ) suffering severely from historic mining and smelting activities, peripheral zone (PZ) that is relative slightly affected by historic mining and smelting activities, and background zone (BZ) unaffected by such past anthropogenic activities.

2.2. Collection and preparation of soil samples

Total 29 topsoil samples (0–20 cm depth) were collected after the top surficial soil (0–5 cm) was discarded, using a stainless-steel shovel in the Lanmuchang area. As shown in Fig. 1, 12 samples were randomly collected from CZ area, 9 samples from PZ area and 8 samples from BZ area. At each sampling site, 5 sub-samples were taken from an area of 4–5 m^2, and mixed together to composite one soil sample. All soil samples were placed in polyethylene bags and transported to the laboratory. In the laboratory, the collected soil samples were air-dried, gently crushed and sieved through 2-mm nylon sieve to remove stones, coarse material and other debris. Portions of each sieved soil samples, divided through quartering method, were then ground by an agate grinder to 80-mesh (<180 μm) powder for element analysis.

2.3. Determination of total concentrations of metal(loid)s in soil samples

For total concentrations of Tl and other metal(loid)s, approximately 50 mg of the sieved soil samples (<180 μm) were weighted and digested using a heated mixture of concentrated acids (15 mL of 15 M HNO_3 and 5 mL of 10 M HF), and the total concentrations of Tl, Hg, As, Sb and other trace elements were determined using an inductively coupled plasma mass spectrometry (ICP-MS, ELAN DRC-e, Perkin-

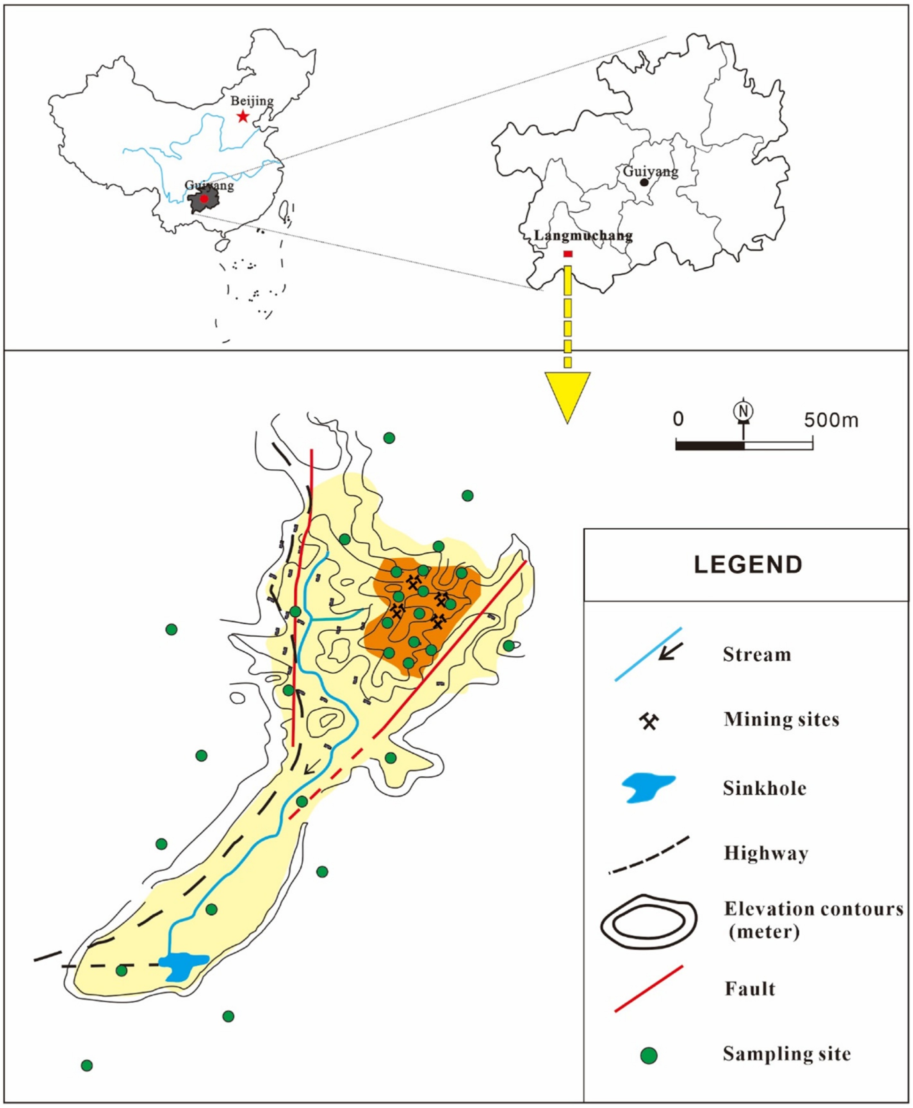

Fig. 1. Study area and sampling sites.

Elmer, USA) (Ning et al. 2015). The detection limits for Tl, Hg, As and Sb was 0.02, 0.01, 0.2, and 0.05 mg kg^{-1}, respectively, which is significantly lower than their concentrations in this study. Standard references of soils, GBW07403 and GBW07408 (National Institute of Standard Materials, China) were used to control the analysis quality. The analytical precision was determined by standard quality assurance/quality control procedures using duplicates, blanks, internal standards (Rh at 500 μg L^{-1}) and reference samples, and the result was better than ± 10% (Qi et al. 2000).

2.4. Measurement of bioaccessibility of Tl, Hg, As, Sb in soil samples

The bioaccessibility test according to SBET was performed according to the protocol recommended by the US EPA (Oomen et al. 2002; USEPA 2008), with little modification. The extraction fluid contained 0.4 M glycine (30.03 g glycine dissolved in 250 mL deionized water), and was adjusted to pH 1.5 ± 0.05 by reagent grade concentrated HCl and finalized by diluting to l L using deionized water adjusted pH to 1.5 ± 0.05. Detailed extraction procedures are as follow: 0.4 g of the sieved soil sample (< 180 μm) was placed in 50 mL centrifuge tube, 40 mL above-mentioned extractant was added, and the mixture was shaken at 60 rpm for 1 h at 37 °C, centrifuged at 2500*g* for 30 min, and then the supernatant was filtered through syringe filter with 0.45 μm nitrocellulose membrane. After determination of pH, the extracted solution samples were stored at 4 °C in a refrigerator. The analysis for total concentrations of Tl, Hg, As and Sb in the extracted solution was performed using ICP-MS as the method described in Section 2.3 for total concentrations of metal(loid)s.

A PBET test, a two-phased (including gastric phase and intestinal phase) *in vitro* extraction method, as described by Ruby et al. (1996) with little modification, was also adopted to quantify the bioaccessibility of metal(loid)s. In the first stage (PBETG), 0.4 g of the sieved soil sample (<180 μm) was extracted using 40 mL simulated gastric solution (pH adjusted to 1.5 ± 0.05 using concentrated HCl), consisting of 1.25 g pepsin, 0.50 g sodium malate, 0.50 g sodium citrate, 420 μL lactic acid, 500 μL acetic acid and 1 L deionized water. The mixture was then shaken at 60 rpm for 1 h at 37 °C, centrifuged at 2500g for 30 min, and then, 2.0 mL of the supernatant was collected and filtered through syringe filter with 0.45 μm nitrocellulose membrane. 2.0 mL of the original gastric solution was supplemented into the same tube to retain the initial solid: solution ratio (1:100 mg L^{-1}). In the second stage (PBETI), 70 mg bile salts and 20 mg pancreatin were added into the sample tube, and the solution pH was adjusted to 7.0 with solid $NaHCO_3$ salt. After standing for 30 min, the sample was placed back on shaker for 4 h at

37 °C, then centrifuged at 2500g for 30 min, and finally, 2 mL supernatant was collected and filtered (0.45 μm filter). The concentrations of metal(loid)s in extracts collected in two stages were also determined by ICP-MS.

The bioaccessible concentrations of metal(loid)s in soil samples were expressed as *M* in mg kg^{-1} (ppm), and the bioaccessibility of metal(loid)s were expressed as BAF in % amount of total concentrations:

$$\mathrm{BAF}\ (\%) = \frac{M}{C} \times 100 \tag{1}$$

where *C* is the total concentration of metal(loid)s in soil sample. For PBET test, its bioaccessibility is the sum of the bioaccessibility values obtained through PBET-gastric simulation extraction (PBETG) and PBET-intestinal extraction (PBETI).

2.5. Human health risk assessment

Quantitative health risk assessment of exposure to metal(loid)s in soils *via* oral ingestion for adults and children were estimated by the model recommended by the USEPA (2011). The traditional chronic daily intake (CDI, mg kg^{-1} day^{-1}) of individual metal(loid) through incidental ingestion of soil was calculated using follow formula:

$$\mathrm{CDI} = \frac{C \times IR \times EF \times ED}{BW \times AT} \times 10^{-6} \tag{2}$$

where C is the total concentration of metal(loid) (mg kg^{-1}), IR is the soil ingestion (mg day^{-1}, 100 for adult and 200 for children), EF is the exposure frequency (day year^{-1}, 250), ED is the exposure duration (years, 25 for adults and 6 for children), BW is the body weight (kg, 61.8 for adults and 15 for children), and AT is the average time of exposure (days, AT = ED × 365) (USEPA 2011).

The non-cancer risks of Tl, Hg, As and Sb were assessed by calculating the hazard quotients (HQs). The HQ and carcinogenic risk (CR) for individual metal(loid) were calculated by the following equations (USEPA, 2007):

$$\mathrm{HQ} = \frac{CDI}{RfD} \times BAF \tag{3}$$

$$\mathrm{CR} = CDI \times BAF \times SF \tag{4}$$

where RfD is the oral reference dose (mg kg^{-1} day^{-1}, 1.00E-05 for Tl, 1.60E-04 for Hg, 3.00E-04 for As and 4.00E-04 for Sb), SF is the slope factor (unitless, 1.50E+00 for As) (USEPA 2011). In this study, we only evaluated the carcinogenic risk for As, because Tl has no carcinogenicity for human, and for Sb and Hg, although they had been classified into the substances with potential carcinogenicity for human, it is presently lack of data on SF for Hg and Sb.

Because exposure to two or more pollutants may lead accumulative or synergetic effects, the sum of HQs for all pollutants can be represented as total hazard risk (HI) for a specific exposure pathway combination using the equation as follow:

$$HI = \sum HQ_i \tag{5}$$

In the study, HI is a measure of the potential risk of noncarcinogenic effects from a mixture of Tl, Hg, As and Sb. If HI (or HQ) < 1, it indicates no significant risk of non-carcinogenic effects, if HI (or HQ) between 1 and 10, it means possible adverse health effects occur, if HI (or HQ) is >10, it means that there are highly adverse health effects. When the values of CR are greater than 10^{-4}, it indicates human tolerance is exceeded, when CR is lower than 10^{-6}, it means no cancer risk exists; When CR between 10^{-6} and 10^{-4}, it suggests that the cancer risk is within the acceptable range (Li et al. 2014; Han et al. 2020).

2.6. Statistical analysis

All the processing and statistical analysis of the data were performed using Microsoft Excel 2010 (Microsoft Inc., USA) and the SPSS statistical package (version 18.0 for Windows, SPSS Inc., USA). One-way analysis of variance (ANOVA) at the level of significance of 95% ($p < 0.05$) was used to determine the significances in concentrations, bioaccessibilities and human health risks. The figures in this paper were drawn by Microsoft Excel 2010 and CorelDRAW2019 (Corel Inc., Canada).

3. Results and discussion

3.1. Total concentrations of metal(loid)s in soils

The results for total concentrations of metal(loid)s (Tl, Hg, As, Sb, Cu, Cr, Ni, Zn, Pb and Cd) in 29 soil samples collected from Lanmuchang area were characterized in Table 1. The average total Tl content was 44.8 ± 67.7 mg kg^{-1}, with the wide range of concentration (0.38–231 mg kg^{-1}). It notably excesses the Chinese background value (0.58 mg kg^{-1}) and regional background value (0.794 mg kg^{-1}) by more than two orders of magnitude, and it is also higher than the Canadian environmental quality guideline value for Tl (1 mg kg^{-1}). Moreover, compared to Tl contents in soils from other places in literature, such as soils from a Tl-rich pyrite processing area in South China (5–15 mg kg^{-1}) (Yang et al., 2005), the Verdugal mining area in Madrid, Spain (1.30–2.65 mg kg^{-1}) (Gomez-Gonzalez et al. 2015), the Southern Bohemia with high Tl background, Czech (Vanek et al., 2009), the Silesian-Craeowian Zn—Pb mine area (8.8–27.8 mg kg^{-1}) (Lis et al. 2003), and a metallurgical zone in Mexico (Cruz-Hernandez et al. 2018), Tl contents in soils from Lanmuchang area are still considerably higher. Generally, Tl contents could decrease with distance or be impacted from the mining/mineralized site. In this study, the average Tl contents in CZ area (95.8 ± 80.4 mg kg^{-1}) were considerably higher ($p < 0.05$) than that in PZ area (15.5 ± 20.7 mg kg^{-1}) and BZ area (1.38 ± 1.15 mg kg^{-1}), with the order of CZ > PZ > BZ. It suggested that CZ and PZ area were suffered serious Tl contamination by mining activities and sulphide mineralization. And Tl contents in BZ was a little higher than the regional value, indicating that BZ area is a geological background area with high Tl content, and is mainly affected by geogenic Tl. These findings are consistent with previous studies (Xiao et al. 2004a; Lin et al. 2020).

Mercury and As, similar with Tl, had elevated total contents, ranged from 0.58 to 906 mg kg^{-1} (mean value 110 ± 193 mg kg^{-1}), and from 8.07 to 306 mg kg^{-1}(mean value 84.4 ± 89.2 mg kg^{-1}), respectively. The average contents of both Hg and As were not only extensively higher than the Chinese background values (0.065 and 11.2 mg kg^{-1} for Hg and As, respectively) and regional background values (0.110 and 20 mg kg^{-1} for Hg and As, respectively), but also exceeded the risk screening values of Chinese farmland soil (4.0 and 40 mg kg^{-1} for Hg and As, respectively). Moreover, both the total contents of Hg and As in different area were in same order of CZ > PZ > BZ with Tl. These indicated that soils in Lanmuchang area distinctly enriched Hg and As, and extensively impacted by local historic mining activities. More importantly, the elevated contents of Hg and As could cause seriously potential human health risk. In addition, it is noteworthy that a significantly positive correlation was found among Tl, Hg and As ($r = 0.748$, $p < 0.01$ for Tl *vs* Hg; $r = 0.727$, $p < 0.01$ for Tl *vs* As, and $r = 0.837$, $p < 0.01$ for Hg *vs* As) (Table 2), indicating that Tl, Hg and As could be originated from same sources. Our previous research had pointed out the weathering and mining effects of minerals containing elevated contents of Tl, Hg and As, such as lorandite ($TlAsS_2$), christite ($TlHgAsS_3$), realgar (As_4S_4), orpiment (As_2S_3) and Cinnabar (HgS) (Xiao et al. 2004a, 2012).

Besides, as shown in Table 1, the mean values of Sb, Cu, Cr, Ni, Zn, Pb and Cd total concentrations were 14.8 ± 24.8, 89.6 ± 31.9, 117 ± 63.8,

Table 1
Total contents of metal(loid)s in soil samples from Lanmuchang area (mg kg^{-1}).

Sampling sites		Tl	Hg	As	Sb	Cu	Cr	Ni	Zn	Pb	Cd
CZ($N = 12$)	Mean	95.8	242	152	16.2	83.6	88.8	41.5	83.0	44.6	0.34
	SD	80.4	246	104	31.7	30.5	71.0	21.9	36.3	56.3	0.19
PZ($N = 9$)	Mean	15.5	28.7	44.2	20.8	112	135	73.6	156	28.8	0.28
	SD	20.7	46.6	27.9	25.0	33.1	51.7	6.96	64.2	13.9	0.10
BZ($N = 8$)	Mean	1.38	4.67	28.1	5.81	73.1	138	54.9	103	20.3	0.30
	SD	1.15	6.13	18.4	5.15	17.0	54.5	9.10	28.8	3.08	0.07
All soils ($N = 29$)	Mean	44.8	110	84.4	14.8	89.6	117	55.2	111	33.0	0.31
	SD	67.7	193	89.2	24.8	31.9	63.8	20.3	53.8	37.6	0.14
	Min	0.38	0.58	8.07	0.93	29.2	51.7	10.8	31.5	14.6	0.09
	Max	231	906	306	115	170	312	86.8	319	221	0.79
Background value in China[a]		0.58	0.065	11.20	1.06	22.60	61.00	26.90	74.20	26.00	0.097
Background value in Guizhou[a]		0.712	0.110	20.0	2.24	32	95.9	39.1	86.9	35.2	0.659
Risk Screening value[b]		1[c]	2.4	40	10[d]	100	200	100.0	250	120	0.3

SD: standard deviation, Min: minmum, Max: maximum.

[a] Referenced from Qi et al. (1992) and Wang et al. (1995).

[b] Referenced from MEEC (2018).

[c] The Canadian environmental quality guideline for Tl in soil, referenced from CCME (2003).

[d] Referenced from Toth et al. (2016).

55.2 ± 20.3, 111 ± 53.8, 33.0 ± 37.6, 0.31 ± 0.14 mg kg^{-1}, respectively. Although exceeding the Chinese background values and regional background values of corresponding elements, these values (except Sb) were much lower than the relevant metal(loid)s' risk screening values of Chinese farmland soil, indicating that Cu, Cr, Ni, Zn, Pb and Cd are not the main pollutants, and their ecological risk or human health risk is very low, or even can be ignored in Lanmuchang area. Yet, the mean value of Sb was higher than the guideline value (10 mg kg^{-1}) recommended by the Ministry of the Environment, Finland, suggesting that potential ecological risk or health risk could be induced by Sb in Lanmuchang area. Additionally, except Pb, the mean contents order of Sb, Cu, Cr, Ni, Zn, Pb and Cd in different areas is ruleless and different from Tl, Hg and As, eg, PZ > CZ > BZ for Sb and Cu, BZ > PZ > CZ for Cr, PZ > BZ > CZ for Ni and Zn, and CZ > BZ > PZ for Cd.

3.2. The bioaccessibilities of Tl, Hg, As and Sb in soils

The bioaccessible concentrations and bioaccessibilities of Tl, Hg, As and Sb using two *in vitro* chemical extraction tests (SBET and PBET) were shown in Fig. 2, and the relationship between the total and bioaccessible concentrations of Tl, Hg, As and Sb are expressed as correlation coefficients in Table 2.

For SBET, the average bioaccessible concentrations of Tl, Hg, As and Sb were 1.73 ± 2.73, 0.45 ± 0.51, 2.18 ± 2.66 and 0.06 ± 0.09 mg kg^{-1}, respectively. Similarly, For PBET, the bioaccessible concentrations of Tl, Hg, As and Sb were also low, with the average values of 4.24 ± 5.90, 2.05 ± 3.04, 7.95 ± 9.58 and 0.30 ± 0.41 mg kg^{-1}, respectively. In general, the bioaccessible concentrations of Tl, Hg, As and Sb for most samples were low, and the bioaccessible concentrations of Tl and As were relatively higher than those of Sb and Hg (Fig. 2A). However, interestingly, for bioaccessibility by SBET and PBET, these four elements showed different variation trends from their bioaccessible concentrations. Based on data of SBET bioaccessibility, Tl had the highest average value (8.38 ± 5.68%), sequentially followed by Hg (5.70 ± 7.14%), As (4.15 ± 4.11%) and Sb (0.78 ± 0.61%). And for PBET bioaccessibility, these four elements showed the following decreasing order of Hg (11.8 ± 13.2%) > Tl (11.4 ± 6.59%) > As (10.4 ± 9.31%) > Sb (3.70 ± 2.54%) (Fig. 2B). It suggested that Tl, As and Hg, compared to Sb, have much higher bioaccessibility and were much more easily adsorbed in gastrointestinal tract once ingested, because Tl, As and Hg in surface soils of Lanmuchang mainly originated from anthropic sources impacted by historic mining and smelting, and thus they were more mobile and bioaccessible than those from geological sources. For all these four metal(loid)s, both their average PBET bioaccessible concentrations and bioaccessibility were higher than those of SBET. Li et al. (2014) also reported similar results for As and Sb in soils from Xikuangshan Sb mine, Hunan, China. Moreover, in different areas, both the bioaccessible concentrations and bioaccessibility of Tl, Hg, As and Sb were different. Among three different sampling areas, CZ had the highest SBET and PBET bioaccessible concentrations, followed by PZ and CZ. And significantly positive correlation between total and bioaccessible concentrations of each metal(loid) was indicated by the high value of the correlation coefficient (Table 2), suggesting that total concentration of metal(loid)s is an important control factor for their bioaccessible concentration, which is consistent with previous study (Li et al. 2014). However, for bioaccessibility of Tl, Hg, As and Sb by SBET and PBET, an opposite order was shown as BZ > PZ > CZ, suggesting that higher bioaccessibility values of Tl, Hg, As and Sb were found in zones with relative lower total contents. As we known, bioaccessibility of metal(loid) in soils is very complex and varies greatly depending on many factors including the geochemical nature of metal (loid), total concentration, source, soil characteristics (eg. pH, electronic conductivity, text and organic matter content), land use type and so on (Li et al. 2014; Wu et al. 2015; Xing et al. 2019; Han et al. 2020). Thus, site with low concentrations of metal(loid)s may have higher bioaccessibility.

In this study, the SBET method is a simplified form of the PBET and just a one-step extraction to simulate gastric condition, without including an intestinal compartment with more neutral pH levels. Both the SBET and PBETG (PBET-Gastric) can simulate the human gastric extract, the pH of these two gastric extraction solutions were adjusted to the same values in this study, but their components in two extraction solutions were distinctly different. Therefore, differences of the bioaccessible concentrations and bioaccessibility of Tl, Hg, As and Sb between SBET and PEBTG could occur. In fact, although no significant differences ($p > 0.05$) were obtained, the average bioaccessible concentrations of Tl (2.03 ± 3.08 mg kg^{-1}), As (3.07 ± 3.88 mg kg^{-1}) and Sb (0.12 ± 0.18 mg kg^{-1}) extracted by PBETG test were a bit higher than those by SBET while an opposite trend occurred for Hg (0.23 ± 0.26 mg kg^{-1} for PBETG and 0.45 ± 0.51 mg kg^{-1} for SBET) (Fig. 2A). For the bioaccessibility in gastric, Tl, Hg, As and Sb can be divided into two group, one group includes Tl and Hg, the average SBET bioaccessibility of which were relatively higher compared to PBETG (6.14 ± 4.10% for Tl and 2.84 ± 3.86% for Hg), but the other group including As and Sb showed PBETG (4.26 ± 5.13% for As and 1.48 ± 1.04% for Sb) exceeded SBET (Fig. 2B). Unfortunately, no relevant soil biaccessibility data are available in literature for Tl and Hg, and this study was also the first investigation of the simulated gastric bioaccessibility in Lanmuchang area. Nevertheless, it is widely known that both Tl and Hg are more mobile in relatively acidic condition, and compared with

Table 2
Pearson correlations between biaccessible concentrations and total contents of metal(loid)s.

		Tl					As					Sb	
		Total	SBET	PBETG	PBETI	PBET	Total	SBET	PBETG	PBETI	PBET	Total	SBET
Tl	Total	1											
	SBET	**0.941****	1										
	PBETG	**0.919****	**0.975****	1									
	PBETI	**0.878****	**0.856****	**0.909****	1								
	PBET	**0.919****	**0.946****	**0.979****	**0.975****	1							
As	Total	**0.727****	**0.716****	**0.733****	**0.671****	**0.715****	1						
	SBET	**0.649****	**0.625****	**0.549****	**0.583****	**0.574****	**0.550****	1					
	PBETG	**0.852****	**0.680****	**0.678****	**0.746****	**0.720****	**0.502****	**0.933****	1				
	PBETI	**0.919****	**0.790****	**0.810****	**0.732****	**0.787****	**0.692****	**0.822****	**0.901****	1			
	PBET	**0.914****	**0.776****	**0.777****	**0.757****	**0.781****	**0.632****	**0.892****	**0.963****	**0.984****	1		
Sb	Total	−0.079	−0.020	−0.083	−0.067	−0.089	0.053	0.258	0.103	0.089	0.097	1	
	SBET	0.239	0.248	0.245	0.403	0.319	0.166	**0.713****	**0.684****	**0.488****	**0.578****	**0.428***	1
	PBETG	0.110	0.185	0.120	0.184	0.142	0.056	**0.715****	**0.459***	**0.386***	**0.425***	**0.554****	**0.940****
	PBETI	0.079	0.170	0.094	0.133	0.102	0.053	**0.688****	**0.405***	0.368	**0.393***	**0.574****	**0.927****
	PBET	0.089	0.175	0.102	0.152	0.117	0.053	**0.701****	**0.426***	0.374	**0.404***	**0.567****	**0.935****
Hg	Total	**0.748****	**0.813****	**0.807****	**0.620****	**0.731****	**0.837****	**0.459***	**0.470***	**0.708****	**0.629****	−0.097	0.090
	SBET	0.135	0.020	0.047	0.206	0.113	0.274	0.212	0.254	0.181	0.215	0.271	0.231
	PBETG	0.302	0.355	0.270	0.128	0.195	**0.398***	**0.487***	0.316	**0.378***	0.362	0.093	0.107
	PBETI	**0.388***	**0.539****	**0.501****	**0.469***	**0.489***	0.316	0.220	0.265	0.271	0.275	0.114	0.144
	PBET	**0.405***	**0.557****	**0.513****	**0.471***	**0.496***	0.342	0.258	0.286	0.297	0.300	0.120	0.151
Cu		0.054	0.027	0.115	0.207	0.145	0.115	0.123	0.080	0.080	0.082	0.299	0.329
Cr		**−0.413***	−0.371	**−0.407***	−0.363	−0.381	**−0.368***	−0.140	−0.256	−0.290	−0.284	**0.650****	0.123
Ni		**−0.416***	**−0.424***	**−0.383***	−0.303	−0.345	−0.358	−0.149	−0.260	−0.317	−0.302	0.327	0.219
Zn		−0.252	−0.092	−0.198	−0.136	−0.182	−0.179	0.370	0.021	−0.033	−0.012	**0.369***	**0.703****
Pb		0.353	**0.535****	**0.396***	**0.549****	**0.476***	**0.448***	**0.550****	0.328	0.292	0.314	0.012	0.203
Cd		−0.076	−0.068	−0.116	−0.074	−0.108	−0.171	0.261	0.158	−0.017	0.054	−0.141	0.125

[*] Statistical significance at the probability level of $p < 0.05$.

[**] Statistical significance at the probability level of $p < 0.01$.

organic acid used in PBETG test, hydrochloric acid has more strong digestion ability (Lin and Nriagu, 1999; Park et al. 2018), so the SBET bioaccessibility of Tl and Hg were higher than PBETG. For As and Sb, other researchers had reported that SBET bioaccessibility was higher that PBETG bioaccessibility, and inferred that Fe, Al and Mn (hydr)oxides in soils are the crucial decisive factors for their bioaccessibility (Li et al. 2014; Cao et al. 2020). We surmised that such different results may be induced by the difference of soil constitutions among different sites.

In two phases of PBET, the bioaccessible concentrations of Tl (4.11 ± 3.76 mg kg^{-1}), Hg (0.23 ± 0.26 mg kg^{-1}), As (3.07 ± 3.88 mg kg^{-1}) and Sb (0.12 ± 0.18 mg kg^{-1}) in gastric environment for almost all samples were either approximate to, or lower than those (2.05 ± 2.89 mg kg^{-1} for Tl, 1.82 ± 2.97 mg kg^{-1} for Hg, 4.87 ± 5.94 mg kg^{-1} for As and 0.18 ± 0.23 mg kg^{-1} for Sb, respectively) in intestinal environment. However, as exhibited in Fig. 2B, Tl had much higher bioaccessibility value (6.14 ± 4.10%) in gastric phase than that (4.98 ± 2.74%) in intestinal phase while Hg, As and Sb showed opposite trend, with the average values of 2.84 ± 3.86%, 4.26 ± 5.13% and 1.48 ± 1.04% in gastric system, and 8.98 ± 10.5%, 6.17 ± 4.44% and 2.23 ± 1.55% in intestinal system, respectively. For Tl, to our knowledge, no research on its soil bioaccessibility was reported, and hence the aforementioned studies may not provide any clear explanations for such increase of Tl bioaccessibility from gastric phase to intestinal phase, but it had been proposed that the increase in pH from gastric phase (1.5) to intestinal phase (7.0) may result in the adsorption, complexation or co-precipitation of Tl due to the lower stability of some other stable metal oxide-Tl or organic Tl complexes (Lin and Nriagu, 1999). For Hg, although some previous studies had reported similar results (Lu et al. 2017), the reason of Hg bioaccessibility in intestinal phase exceeding that in gastric phase were still unknown. For As and Sb, some contradictory results had been reported in previous researches. Cao et al. (2020) introduced similar results of an increasing of As and Sb bioaccessibility from gastric phase to intestinal phase. However, Li et al. (2014) found that Sb (6.62 ± 6.37%) and As (7.83 ± 9.83%) bioaccessibility values in gastric environmental are higher than those in the intestinal environment (Sb: 2.40 ± 2.01%, As: 3.03 ± 3.53%). Besides, Denys et al., 2009, 2012 reported no difference between the gastric and the intestinal bioaccessibility values of As and Sb, and they attributed this to that Sb occurred as the free anionic form and there was no complexation components for Sb in the extraction fluids. Additionally, Ruby et al. (1996) pointed out no adsorption and precipitation reactions for As in the intestinal simulation solution with the neutral pH values. Evidently, our results could not be explained by the existing researches, and further study is required.

3.3. Health risk assessment

Taking into consideration that Lanmuchang area is located at remote mountain area, the farmland is around and close to the residential area, and hence it is always an important playing field for local children, therefore, in this study, not only the health risk to adults from ingesting soils was assessed, but risk to children was also evaluated. The HQs, HIs and CRs through soil ingestion for children and adults were calculated, based on total concentration and bioaccessibility of Tl, Hg, As and Sb, and the results were plotted in Figs. 3-5.

For the non-carcinogenic risk, among Tl, Hg, As and Sb, only the average HQ$_{Tl}$ values for children (40.9) and adults (1.77), HQ$_{As}$ for children (2.57) and HQ$_{Hg}$ for children (3.36) based on total contents of metal(loid)s in Lanmuchang area were higher than the safe levels (HQ ≤ 1) (Fig. 3A). It suggested that Tl had the highest non-cancinogenic risk, followed by Hg and As, and Sb had the lowest non-canciogenic risk (0.337E-01 for children and 1.46E-02 for adults). In different sampling areas, the non-carcinogenic risks varied, with the same decreasing order of CZ > PZ > BZ for these four metal(loid)s. Cumulatively, the average HI values to children and adults in all samples were 47.2 and 2.05, which were far higher than 1. And all the average HI values for children in three sampling areas were also higher than 1, with values of 99.8 (CZ), 16.9 (PZ) and 1.42 (BZ), but for adults, just the average HI value in CZ (4.33) exceeded 1. It indicated that high non-carcinogenic risk based on total concentrations of Tl, Hg, As and

Sb			Hg					Cu	Cr	Ni	Zn	Pb	Cd
PBETG	PBETI	PBET	Total	SBET	PBETG	PBETI	PBET						
1													
0.986**	1												
0.995**	**0.997****	1											
−0.036	−0.039	−0.039	1										
0.197	0.167	0.179	0.125	1									
0.132	0.097	0.111	**0.397***	0.175	1								
0.149	0.104	0.119	0.174	0.013	0.242	1							
0.158	0.111	0.127	0.204	0.030	0.323	**0.996****	1						
0.293	0.325	0.313	−0.056	**0.731****	−0.085	0.206	0.194	1					
0.272	0.281	0.280	**−0.422***	−0.113	−0.239	−0.198	−0.213	−0.110	1				
0.310	0.340	0.330	**−0.553****	0.185	−0.132	0.060	0.047	**0.518****	**0.421***	1			
0.733**	**0.764****	**0.754****	−0.349	0.223	0.026	0.192	0.190	**0.556****	0.195	**0.758****	1		
0.155	0.138	0.146	0.276	0.286	0.059	0.163	0.165	0.282	−0.214	−0.257	−0.002	1	
0.193	0.135	0.162	−0.087	0.011	0.091	−0.191	−0.179	−0.286	−0.147	**−0.396***	−0.095	0.148	1

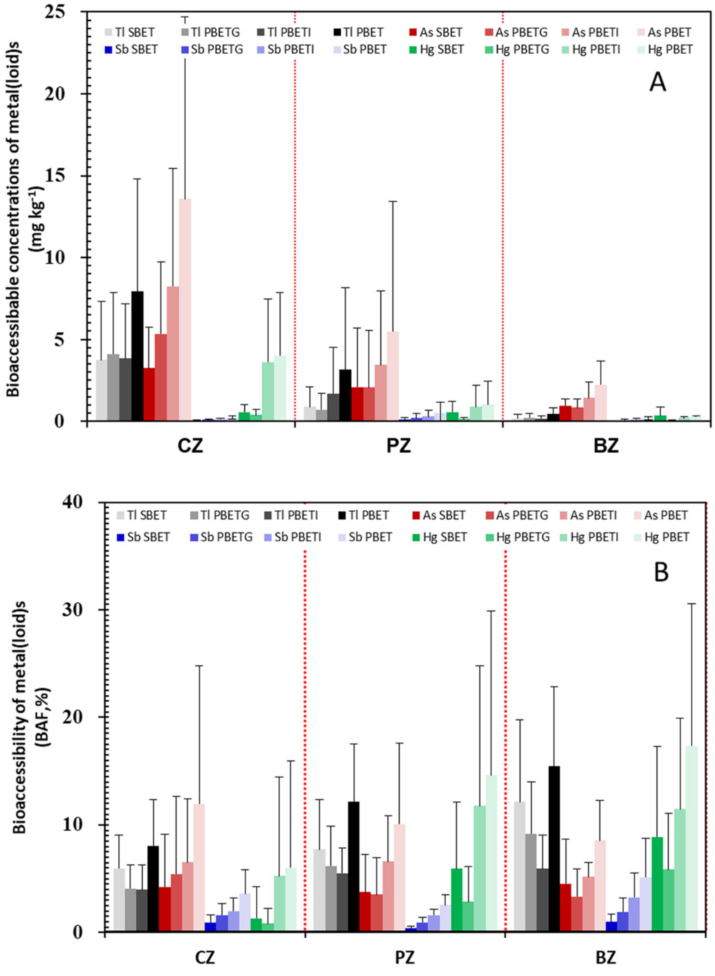

Fig. 2. Bioaccessible concentrations (A) and Bioaccessibility (B) of Tl, Hg, As and Sb in soils from Lanmuchang.

Sb occurred through oral ingestion in Lanmuchang. In addition, among the four metal(loid)s, the HQs of Tl, Hg, As and Sb contributed 86.7%, 7.1%, 5.4% and 0.7% to the HI for all samples, and in different sampling areas, the contribution values of HQ_{Tl}, HQ_{Hg}, HQ_{As} and HQ_{Sb} to the HI varied obviously. The contribution values of HQ_{Tl} and HQ_{Hg} to the HI decreased from 87.6% (CZ) to 52.8% (BZ) and from 7.4% (CZ) to 5.2% (BZ),

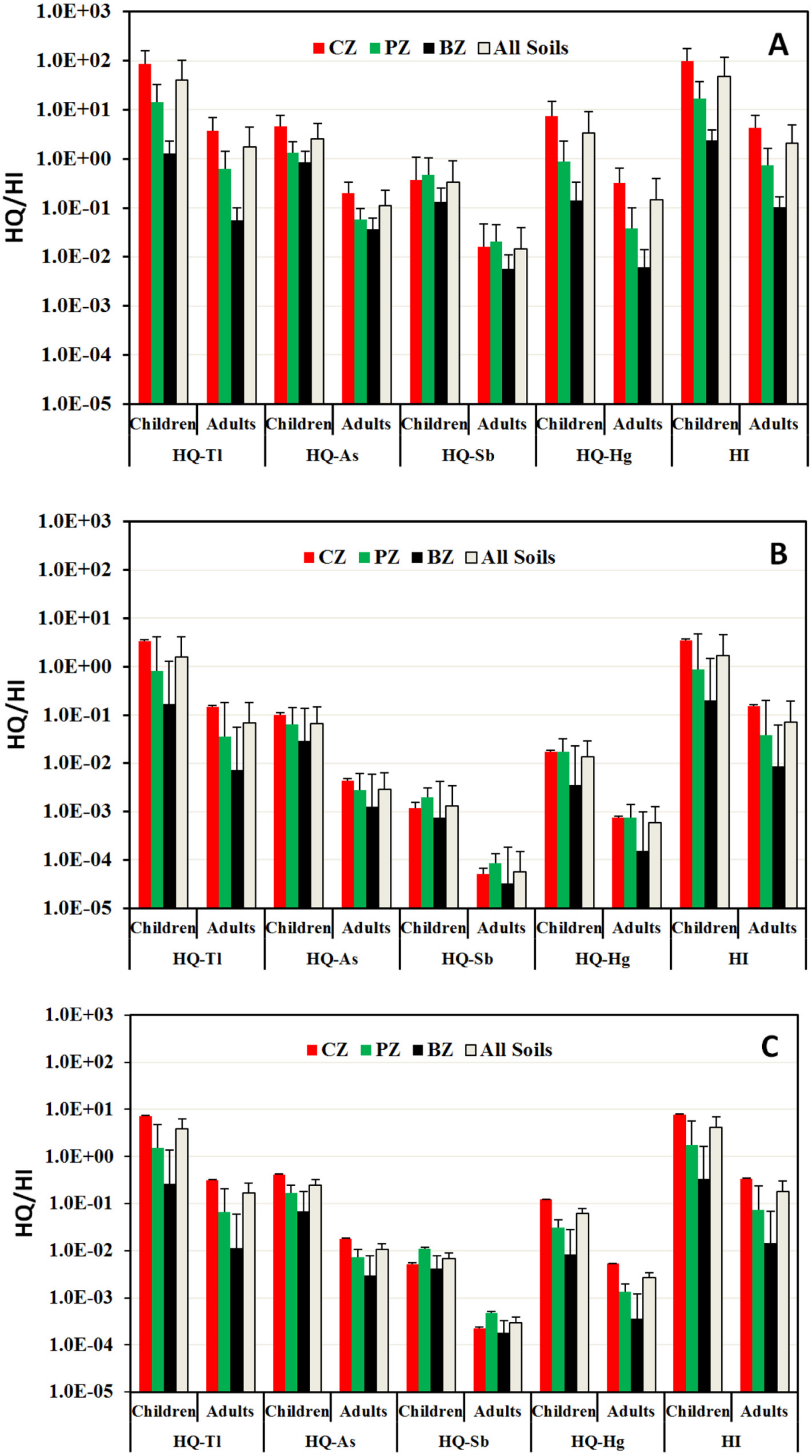

Fig. 3. Hazard Quotient (HQ) values and Hazard index (HI) of metal(loid)s in soils from Lanmuchang, based on total contents of metal(loid)s (A), or considering bioaccessibility of metal(loid)s by SBET (B) and PBET (C).

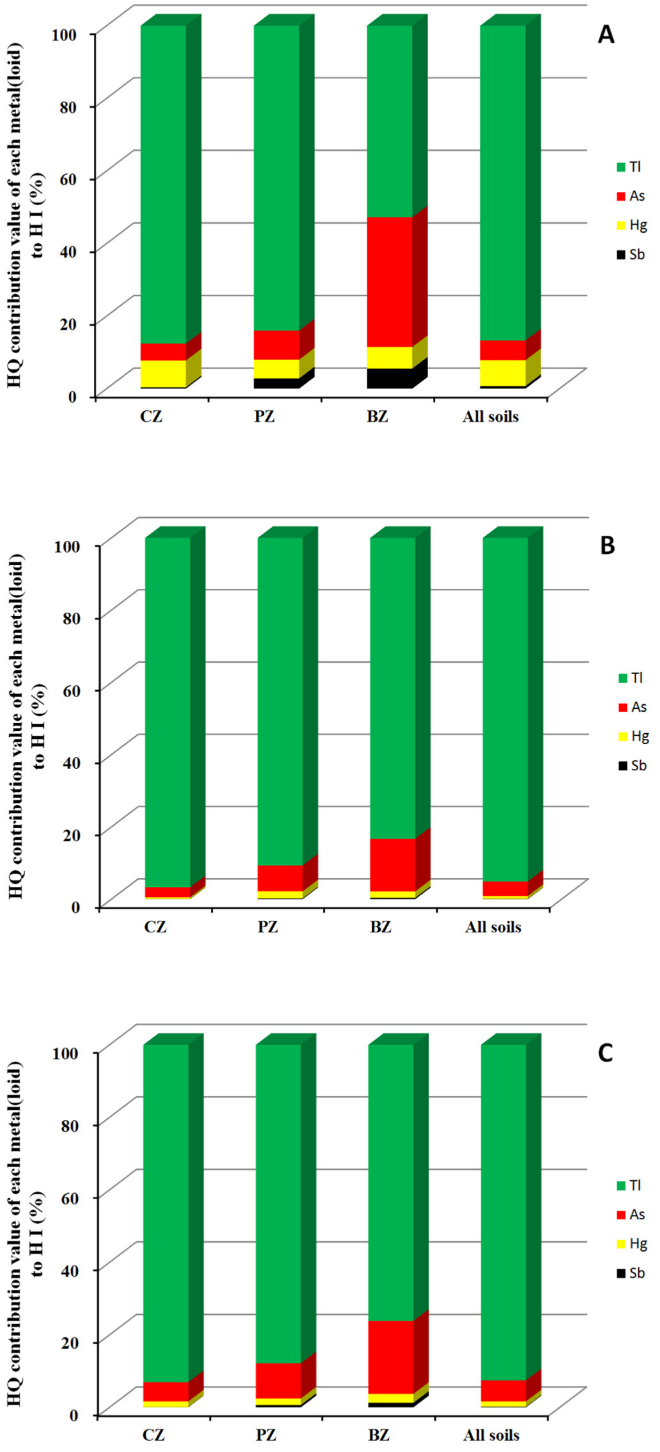

Fig. 4. HQ contribution value of each metal(loid) to HI, based on total contents of metal (loid)s (A), or considering bioaccessibility of metal(loid)s by SBET (B) and PBET (C).

respectively, with the decreasing of pollution degree caused by mining activities while those of HQ_{As} and HQ_{Sb} increased from 4.6% (CZ) to 35.8% (BZ) and from 0.4% (CZ) to 5.5% (BZ), respectively (Fig. 4A). Ma et al. (2020) also recently reported similar research finding in such area. However, since the total metal(loid)s in soils are not absolutely bioaccessible in human gastrointestinal system, the health risk above-mentioned would be overestimated (Luo et al. 2012; Li et al. 2014; Cao et al. 2020). After adjustment by bioaccessibility, the HQ_{Tl}, HQ_{Hg}, HQ_{As} and HQ_{Sb} were significantly reduced. When the SBET bioaccessibility was considered (Fig. 3B), only the average HQ_{Tl} value for children (1.58) for all samples was still slightly higher than 1, and among these different areas, just the average HQ_{Tl} value for children (3.41) in CZ is higher than 1. Meanwhile, the average HI to children and adults for all samples sharply decreased to 1.66 and 7.21E-02, respectively, and the average HI to children and adults in CZ also decreased to 3.53 and 1.53E-01, respectively. Thus, after adjusted by the SBET bioaccessibilty, the toxic risk levels of Tl, Hg, As and Sb decreased one to two orders of magnitude, and the toxic risk values of Hg, As and Sb for all sampling sites were below the dangerous threshold levels, and except less than 28% sampling sites to children, all the toxic risk values of Tl to children and adults were also less than the unaccepted threshold value. Moreover, HQ_{Tl} and HQ_{As} contributed the most (more that 99.0% together) to HI (Fig. 4B). When the PBET bioaccessibility was adopted (Fig. 3C), the HQs and HIs showed similar variation trend with those by SBET. It should be noted that the non-canciogenic risks obtained after adjusted by PBET bioaccessibility were relatively higher ($p < 0.05$), with the average HI of 4.18 (children) and 1.81 E-01 (adults) for all soil samples, compared to those by SBET bioaccessibility. On the contrary, the contribution values of HQ_{Tl} (92.6%) to HI decreased slightly (Fig. 4C). Additionally, for all these four metal(loid)s, the non-carcinogenic risk to children were higher than that to adults. Currently, human health risk assessment based on bioaccessibility of potential toxic element frequently focus on As, Sb, Cd, Pb and Cr. Many existing relevant researches reported similar results with this study. For example, Cao et al. (2020) found the PBET bioaccessibility-corrected HQ and HI values of As, Cd, Sb, Pb, Cu in soils from an e-waste open burning site in Ghana, noticeably decreased, compared to those based on total concentrations. Likewise, Ma et al. (2019) reported the noncarcinogenic risks (HQ and HI) based on the total contents of Cd, Cu, Cr, Ni, Pb and Zn in school/kindergartens soils from different cities of China were much higher than those based on bioaccessibility by SBET. Li et al. (2014) comparatively evaluated human health risks through oral exposure, based on total concentrations and bioaccessibility by SBET and PBET of As and Sb in highly polluted soils around Xikuangshan area, Human, China, and also pointed out that after adjustment by bioaccessibility, the HQ and HI of As and Sb were all significantly reduced. Specifically, they noted that the noncarcinogenic risk of PBET exceeded that of SBET, which is consistent with our results. However, the study for human health risk assessment based on bioaccessibility of Hg and Tl is still rarely reported.

For the carcinogenic risk, the CR_{As} values to children based on the total contents for all samples were much higher than 1.0E-04 with an average value of 1.16E-03, and the CR_{As} values to adults were in the range between 1.0E-06 and 1.0E-04 with an average value of 5.01E-05 (Fig. 5). This suggested that the carcinogenic risks of As to both children and adults through the incidental soil ingestion cannot be acceptable in Lanmuchang area, and specifically the carcinogenic risk level of As to children was extremely serious. For different sampling areas, CZ has the highest CR_{As} values to both children (2.08E-03) and adults (9.03E-05), followed by PZ (6.06E-04 for children and 2.62E-05 for adults) and BZ (3.85E −04 for children and 1.65E-05 for adults). Many previous studies have identified that the carcinogenic risk (CR) of potential toxic element adjusted by SBET or PBET bioaccessibility would dramatically reduce, compared with that based on total concentration of metal (loid)s (Cao et al. 2020; Ma et al. 2019; Huang et al. 2018; Li et al. 2014). Similarly, in this study, the CR_{As} values decreased dramatically when the bioaccessibility of As was incorporated. After adjustment by SBET and PBET, the CR_{As} values to children for almost all samples in the range between 1.0E-06 and 1.0E-04, indicating that the probability of the adverse health effects to children could occur. But for adults, the CR_{As} values were lower than 1.0E-06 in more than 65% (SBET) and 25% (PBET) samples, respectively. According to above results, it is believed that there is a high chance that the non-carcinogenic and

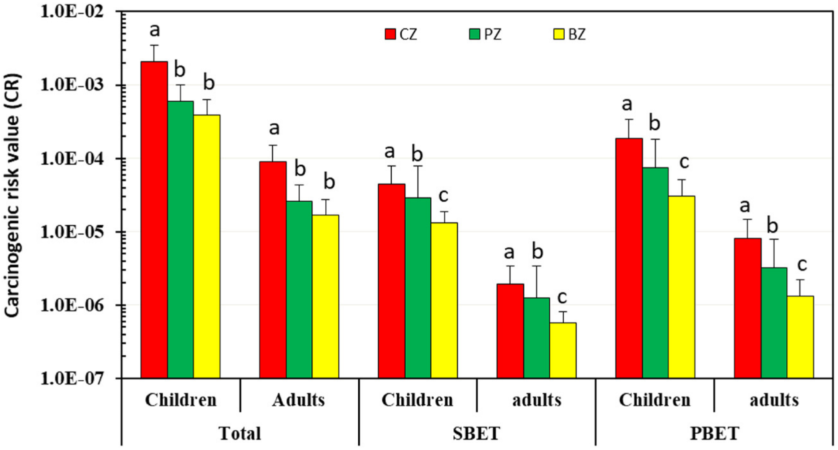

Fig. 5. Carcinogenic risk (CR) values of As to children and adults in soils from Lanmuchang, based on total contents of metal(loid)s, or considering bioaccessibility of metal(loid)s by SBET and PBET. Different letters indicate significant differences ($p < 0.05$) among different areas for children or adults based on total concentrations, PBET or SBET bioaccessibility.

carcinogenic effects to local residents may occur in Lanmuchang area, especially to children living in CZ area, which should need more attention. Furthermore, it is evident that incorporating the bioaccessibility into human health risk assessment can low down the non-carcinogenic risk (Tl, Hg, As and Sb) and carcinogenic risk (As) to children and adults in Lanmuchang area. Therefore, unnecessary excessive concern and remediation cost can be reduced, and even avoided in Lanmuchang, especially in areas with no risk of ingesting contaminated soils by Tl, Hg, As, Sb and other metal(loid)s. Additionally, in this study, it can be inferred that results of health risk assessment adjusted by PBET bioaccessibility were relatively more conservative than those by SBET. This is consistent with many previous studies (eg. Luo et al. 2012; Li et al. 2014; Fernandez-Caliani et al. 2019; Vasiluk et al. 2019; Cao et al. 2020; Han et al. 2020).

4. Conclusions

The total concentrations of Tl, Hg, As, Sb, Cu, Cr, Ni, Zn, Pb, Cd in almost all soil samples from Lanmuchang area were generally higher than the Chinese background values and the regional background values of Guizhou province, but only the average total concentrations of Tl, Hg, As and Sb exceeded the Chinese farmland risk screening values. These indicated that high geological background values of metal(loid)s may occur and the main contaminants were Tl, Hg, As and Sb in Lanmuchang area. The bioaccessibility of Tl, Hg, As and Sb determined by SBET and PBET tests in most samples was lower than 30%, varied greatly, and exhibited marked variance between gastric phase and intestinal phase. In general, the bioaccessibility of these four metal (loid)s by PBET was higher than that by SBET. Tl bioaccessibility in gastric environment was relatively higher than that in intestinal environment, but opposite for Hg, As and Sb. The total contents, geochemical characters and soil constituents may present the main factors affecting the bioaccessibility of Tl, Hg, As and Sb. This study reconfirmed the importance of considering the bioaccessibility of metal(loid)s, rather than the total contents for health risk assessment, it could provide more realistic health risk estimations in Lanmuchang area. Among the four targeted metal(loid)s, Tl and As were the major elements of concern that contributed the most (up to 99%) to the overall health risk to local residents through soil ingestion. Besides, both of the non-carcinogenic risk and the carcinogenic risk to children were higher than adults. Overall, Tl, Hg, As and Sb from the oral ingestion of soils might cause potential toxic risk to the local residents, especially to children in the study area. The application of oral bioaccessibility will provide us more applicable information on human health risk and rational guidelines for future regulation/management of contaminated soils.

CRediT authorship contribution statement

Zengping Ning: Conceptualization, Methodology, Software, Data curation, Writing- Original draft preparation. **Enguang Liu:** Methodology, Software, Data curation. **Dongju Yao:** Methodology, Formal analysis, Data Curation. **Tangfu Xiao:** Writing - review & editing, Supervision. **Liang Ma:** Investigation, Methodology, Formal analysis. **Yizhang Liu:** Data curation, Validation. **Hang Li:** Software, Validation. **Chengshuai Liu:** Writing- Reviewing and Editing, Project administration.

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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