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Comparison and Risk Assessment for Trace Heavy Metals in Raw Pu-erh Tea with Different Storage Years

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Abstract

This research conducted an exploration of the content of microelements (As, Cr, Cd, Pb, Cu, Zn, Mn, and Hg) in raw Pu-erh tea with different storage years. The contents of As, Cr, Cd, Pb, Cu, Zn, Mn, and Hg were 0.14, 0.82, 0.02, 0.52, 14.59, 33.51, 564.02, and 0.01 μg/g, respectively, and were all less than the national standard limit values in China. The target hazard quotients (THQs) of each heavy metal were all lower than 1, and the value of combined risk hazard index (HI) of all to adults was 0.221, which presents no health risk when consumed properly by adults of the raw Pu-erh tea infusions. Interestingly, there was no significant correlation between the heavy metal element (As, Cr, Cd, Pb, Cu, Zn, Mn, and Hg) contents and the THQ values of raw Pu-erh tea samples and storage years; the correlation coefficients (R^2) range from 0.01 to 0.33 and from 0.01 to 0.57, respectively. The result showed that the storage years showed no effect on the exposure risk of heavy metals; the heavy metal elements in tea samples come from the atmosphere and soil.

Keywords Pu-erh tea · Heavy metals · Storage years · Principal component analysis · Potential health risk

Introduction

Pu-erh tea is a uniquely living resources in China and mainly produced in Pu-erh City of Yunnan Province [1]. Pu-erh tea contains a lot of chemical components [2], the main chemical composition of theanine, amino acids, the water-soluble carbohydrates, caffeine, essential minerals, and other major chemical constituents. The main chemical composition is suggested to be beneficial to human health [3]; specifically, it can lower blood cholesterol and triglyceride [4], prevent cardiovascular diseases [5], and protect liver and anticancer [6], antifatigue [7], and antimutagenic potentials [8]. For such health function, Pu-erh tea is favored by more and more people in recent years, especially in Southeast Asia and in France [9].

With the rapid development of industry and economy, anthropogenic heavy metal emissions are increasing [10–12]. Mercury is regarded as the toxic element and has toxic effects on the nervous system, reproductive system, immune system, kidneys, and cardiovascular system [13–16]. Cadmium (Cd) exposure also will increase the risk of cancer (e.g., pancreatic cancer, renal dysfunction) [17–19]. The former researches have indicated that lung cancer patients have high chromium (Cr) in their lung tumors [20, 21]. Lead (Pb) will cause miscarriages [22], neurotoxicity [23], carcinogenicity [24], and hypertension [25], as is toxic to the majority of organ systems, especially for the kidney. Chronic and acute As exposure may cause hypertension and cardiovascular disease [26–28]. Specifically, the inorganic As tends to be far more toxic than organic As [29, 30].

Recently, several studies have conducted a survey and risk assessment for human health of heavy metal pollution in tea [31–33]. Zhang's research shows that the concentrations of Al and Mn in young tea leaves were less than in mature tea leaves, and for mature tea leaves, the hazard index (HI) was 0.970 and the percentage which HI values were above 1 was 38.46% [33]. Fang et al. reported that Cr in tea from South Anhui Province has shown health risks to human [34]. Nkansah et al. found that the target hazard quotient (THQ) values for single heavy metal element of Fe, Zn, As, Cd, and Pb in tea samples (black, green, and white) were all less than 1; however, the HI values of multiple metal elements Fe, Zn, As, Cd, and Pb in unflavored black tea samples of LYLT and

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LCBT brands reach 1.11, which is more than the adverse reaction threshold, and it is very likely that the heavy metals have negative effects on human health [31]. Hongbin et al. found no non-carcinogenic risks by investigating aluminum and microelement heavy metal contents in Pu-erh tea; however, we should pay more attention to the carcinogenic risk of microelement As [35]. Therefore, it is necessary to explore biological enrichment characteristics of trace heavy metal elements in tea and assess human exposure risk.

Unlike other types of tea, which are consumed not long after harvest and process, Pu-erh tastes better with increased storage time [36, 37]. Earlier studies suggest that distinct changes of the compound contents occur in raw Pu-erh tea during the period of storage [17, 36–38]. Storage time influences chemical compositions of tea; the content of moisture and flavonoid compound increased with increasing storage time, while polyphenol (e.g., catechins, caffeine, and amino acid) content decreased gradually [2, 39–41]. However, there still has not any reports about the change of trace and heavy metal contents in raw Pu-erh tea under different storage times.

Therefore, we investigated heavy metal concentrations in raw Pu-erh tea that collected from 2006 to 2018 from China. We selected three kinds of brands of raw Pu-erh tea samples, which are from three major Pu-erh tea–producing areas. Raw Pu-erh tea samples from the same batch were obtained from the same producer with different storage times. We aimed to (1) measure trace heavy metal concentrations in raw Pu-erh tea with different storage times by using inductively coupled plasma-mass spectrometry (ICP-MS); (2) explore the variation of the content of heavy metals in raw Pu-erh tea with different storage times; (3) assess the human safe risks of heavy metals in Pu-erh tea to human by using THQ and HI methods.

Materials and Methods

Study Area

The study areas (Shuangjiang County, Lincang City; Lancang County, Pu'er City; Menghai County, Xishuangbanna Prefecture) were located in Yunnan Province, Southwestern China (Fig. 1). The average altitude of the sampling site (Big Snow Mountain of Mengku) in Shuangjiang County is up to 2300 m. The annual mean air temperature is 20 °C, and the annual mean precipitation ranges from 1000 to 1200 mm. The height of old plant tea average is 20 cm, and the mean diameter at breast height is 40 cm. The range of altitude is from 1100 to 1600 m of the sampling site (Jingmai Mountain) in Lancang County. The annual mean air temperature is 18 °C, and the annual mean precipitation is 1800 mm. The tea trees were grafted on the old tree, and the height of the tea trees range from 3 to 6 cm. The average altitude of the sampling site (Nannuo Mountain) in Menghai County is 1400 m. The annual precipitation ranges from 1500 to 1700 mm, and the average annual temperature ranges from 16 to 18 °C. The tea is bush Pu-erh tea (the mesa Pu-erh tea).

Sample Collection

The Meng library Rong Shi responsibility Limited Company, Lancang Old Tea Limited Company, and Da Yi Tea Group of Yunnan provided old tea trees. These raw Pu-erh tea (001) and raw Pu-erh tea (7542) were produced from 2006 to 2018, respectively. These samples are made of sundried green tea leaves of Yunnan big leave species, and the fresh leaves were sampled and processed by the uniform standards in the same sampling site. Then, samples were stored in a constant temperature and humidity repository; the temperature and humidity in the repository are 20 °C and 60%, respectively, which ensured consistency of storage environment. We collected raw Pu-erh tea samples of 39.

Heavy Metal Analysis

All raw Pu-erh tea samples were dried in a vacuum freeze dryer to a constant weight; then, these samples were grinded and passed a nylon sieve with a bore diameter of 0.074 mm; then, the samples were analyzed in the lab.

About 0.1 g of raw Pu-erh tea samples was placed in a Teflon digestion vessel, and then digested using 5 mL ultrapure HNO_3 in a high-pressure sealed tank that was placed in an electric constant temperature drying oven at 120 °C for 12 h. After cooling, the sample was dried in an electric hot plate, then added with 3 mL ultrapure H_2O_2 and digested again in an electrothermal blowing dry box at 80 °C for 6 h. The digested samples were then measured using inductively coupled plasma-mass spectrometry (ICP-MS) (Agilent HPLC 1290-7700x, USA) according to the Method 6020A [42].

All samples were analyzed in a state key laboratory (State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China).

Analytical Quality Assurance

Method blanks, standard reference material (GBW10020), and sample duplicates were used for quality control. The recoveries of heavy metals for GBW10020 were 90~105%. The relative percentage difference was lower than 6% for heavy metals in duplicate samples.

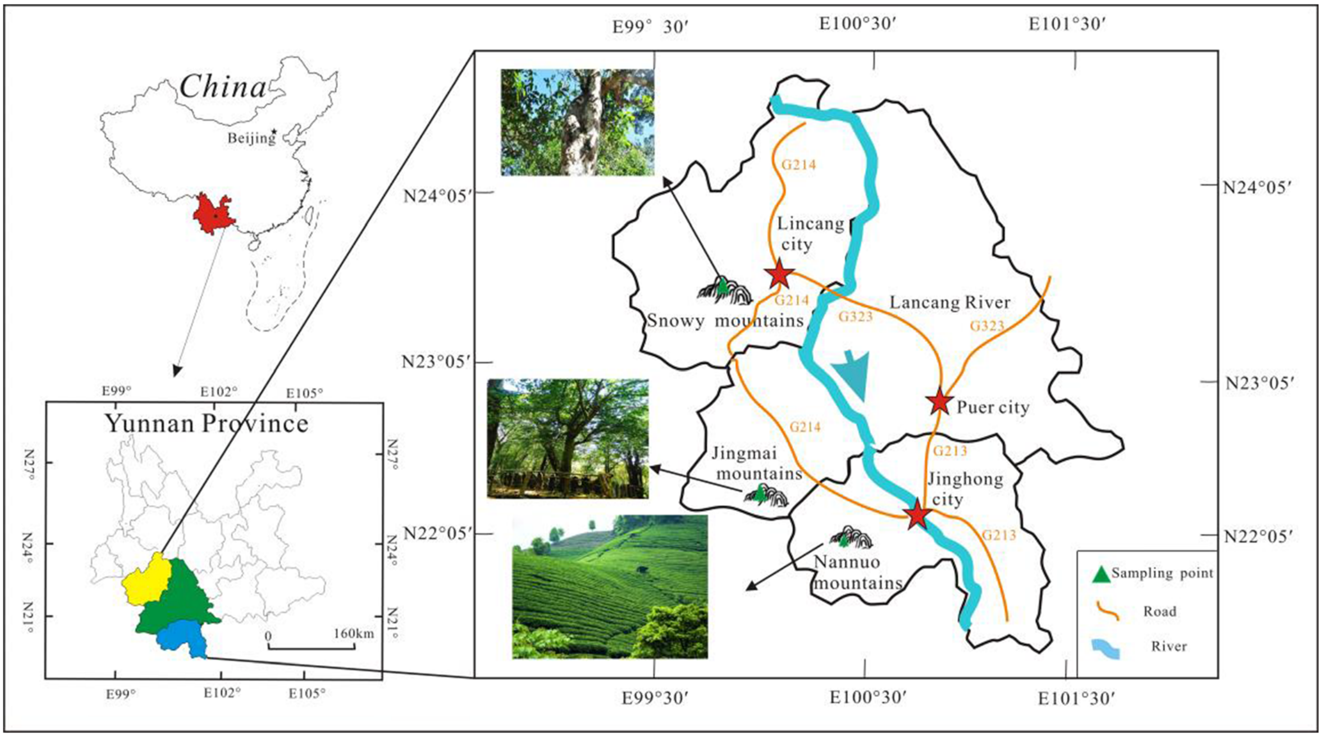

Fig. 1 Study area and location of the sampling points for tea leaves

Human Health Risk Assessment

Estimated Daily Intakes [43]

$$\mathrm{EDI} = (\mathrm{C} \times \mathrm{FIR} \times \mathrm{TR})/(\mathrm{WAB} \times 1000)$$

FIR indicates the tea intake rate, and the unit is g/person/day; previous research has shown that adults' everyday intake is 11.4 g (dry weight) [43], and C is the trace heavy metal content; the unit is mg/kg, and TR indicates the transference rate of trace heavy metal element from tea leaves to tea soup; the unit is %. WAB indicates the average body weight; the adults' average body weight is estimated to be 60 kg [44] (Table 1).

Risk of Single Trace Heavy Metal Element by Consuming Pu-erh Tea [44, 45]

$$\mathrm{THQ} = \mathrm{EDI}/\mathrm{RfD}$$

THQ > 1 indicates that non-carcinogenic effects are risky to the tea-drinker populations (Table 2).

Combined Risk of All Trace Heavy Metal Elements by Consuming Pu-erh Tea [45]

$$\mathrm{HI} = THQ1 + THQ2 + THQ3 + \cdots + THQn$$

Table 1 An explanation of all the acronyms used in this thesis

Acronyms	Units	Explanation
EDI	mg/kg bw/day	Estimated daily intakes
C	mg/kg	The trace heavy metal content
FIR	g/person/day	The tea intake rate
TR	%	The transference rate of trace heavy metal element from tea leaves to tea soup
WAB	kg	The average body weight
RfD	mg/kg bw/day	The oral reference dose
THQ	–	Target hazard quotient
HI	–	Hazard index

Table 2 The transference rates (TR, %) and RfD (mg/(kg day)) values of the studied eight elements

Elements	TR	References	RfD	References
Cu	28.7	[46]	10.0×10^{-4}	[47]
Zn	19.3	[46]	3.6×10^{-3}	[49]
As	16.2	[46]	3.0×10^{-1}	[49]
Mn	22.5	[46]	4.0×10^{-2}	[49]
Cr	42.0	[46]	3.1×10^{-4}	[47]
Cd	6.6	[47]	2.0×10^{-4}	[47]
Pb	19.8	[47]	1.4×10^{-1}	[49]
Hg	45.2	[48]	15.0×10^{-1}	[50]

HI < 1 indicates there is no carcinogenic risk. HI > 1 indicates that heavy metals produce some negative effects on human health. When HI > 10.0, it will be dangerous to human health [51].

Statistical Analyses

Data are analyzed with SPSS Statistics 19, Microsoft Excel 2013, and Origin 8.5. The statistically significant relationships were studied by Pearson's correlation analysis. $p < 0.05$ indicates a statistical significance.

Results and Discussion

Change Trend of Metal Contents in Pu-erh Tea with Different Storage Years

Figures 2 and 3 show the descriptive statistics of the studied microelement heavy metals in raw Pu-erh tea. The paired samples *t* test was used to test the contents of eight heavy metal elements and storage years in all raw Pu-erh tea samples. There was no significant correlation between the heavy metal elements (As, Cr, Cd, Pb, Cu, Zn, Mn, and Hg) in raw Pu-erh tea samples and storage years. The correlation coefficients (R^2) were 0.32, 0.33, 0.25, 0.32, 0.015, 0.03, 0.01, and 0.01, respectively. As shown in Fig. 2, the As, Cr, Cd, and Pb concentrations in raw Pu-erh tea samples in 2006 are 0.23, 1.09, 0.03, and 0.98 μg/g, while 0.11, 0.72, 0.02, and 0.36 μg/g in 2018. The As, Cr, Cd, and Pb concentrations are 1.5 and 2.72 times less than in 2006, while, interestingly, as shown in Fig. 3, the heavy metal elements Cu, Zn, Mn, and Hg in 2006 are comparable with those in 2018. The Cu, Zn, Mn, and Hg concentrations in raw Pu-erh tea samples in 2006 are 15.91, 34.41, 542.39, and 0.03 μg/g, while14.72, 33.94, 585.18, and 0.02 μg/g in 2018. Pollution sources of heavy metal in tea included four aspects: (1) soil base; (2) chemical fertilizer application [52]; (3) machining process [53]; (4) storage process: raw Pu-erh tea is affected by storage environment (e.g., storage containers, warehouse environment); (5) atmospheric quality [54]: raw Pu-erh tea is affected by storage environment (e.g., storage containers, warehouse environment) and atmospheric quality. In the past 20 years, China's rapid economic growth has spurred on the increased demand of energy and mineral resources. Heavy metal emissions are increased year by year caused by human beings at the national level [55]. However, in this study, the heavy metal (As, Cr, Cd, and Pb) contents were reduced with increasing sampling years, which could be related to the sampling area of Lincang, Jinghong, and Pu'er to protect the environment and develop tourism industry in recent years. Moreover, since 2000, China has already banned the use of containing Pb gasoline, which reduced Pb emissions of road. It has been reported that the reduction trends of atmospheric emissions of Cd, Pb, and Hg in Europe in the period from 1980 through 2005, and the tendency of decrease were predicted in this future [56]. Previous studies also showed that atmospheric mercury concentration is declining on the Tibetan Plateau [57]. And the previous studies also reported significantly higher heavy metal element (Pb, Hg, As, Cd, Mn, and Cu) concentrations in twigs and leaves of *Abies fabri* in 1999 than in 2014 [58]. The recent decline heavy metal levels in atmosphere may explain the decline heavy metal concentrations for raw Pu-erh tea with different storage years. This is the very reason which heavy metal contents of tea samples in 2018 are less than in 2006.

As, Cr, Cd, Pb, Cu, Zn, Mn, and Hg concentrations in tea ranged 0.10~0.23, 0.48~1.23, 0.02~0.05, 0.26~0.98, 14.34~15.91, 32.03~34.41, 517.53~784.00, and 0.01~0.03 μg/g, respectively. These values are comparable with previous results about Pu-erh tea samples from Pu-erh City [35] and other types of tea from Guizhou Province [33]. However, interestingly, the value of our results of Pu-erh tea is under the selected tea products (black tea, green tea, and white tea) from the Ghanaian market [31]. In addition, heavy metal concentrations in this study of all samples were below the standard, which the heavy metal concentration of Pb is 5.0 μg/g and those of the elements Cu, As, Hg, Cd, and Cr are 30, 2.0, 0.3, 1.0, and 5.0 μg/g, respectively, recommended by the National Food Safety Standard [59] and the Department of Agriculture tea leaves microelement heavy metal safety standards [60, 61] in China, indicating a free risk of exposure for tea drinkers (Table 3).

Principal Component Analysis

The principal component analysis (PCA) is a statistical method that converts a set of potentially correlated variables into a set of linearly unrelated variables by orthogonal transforms. Principal component analysis (PCA) is useful for determining the correlation among elements and number of principal components. Lastly, it is used to identify the source of the data

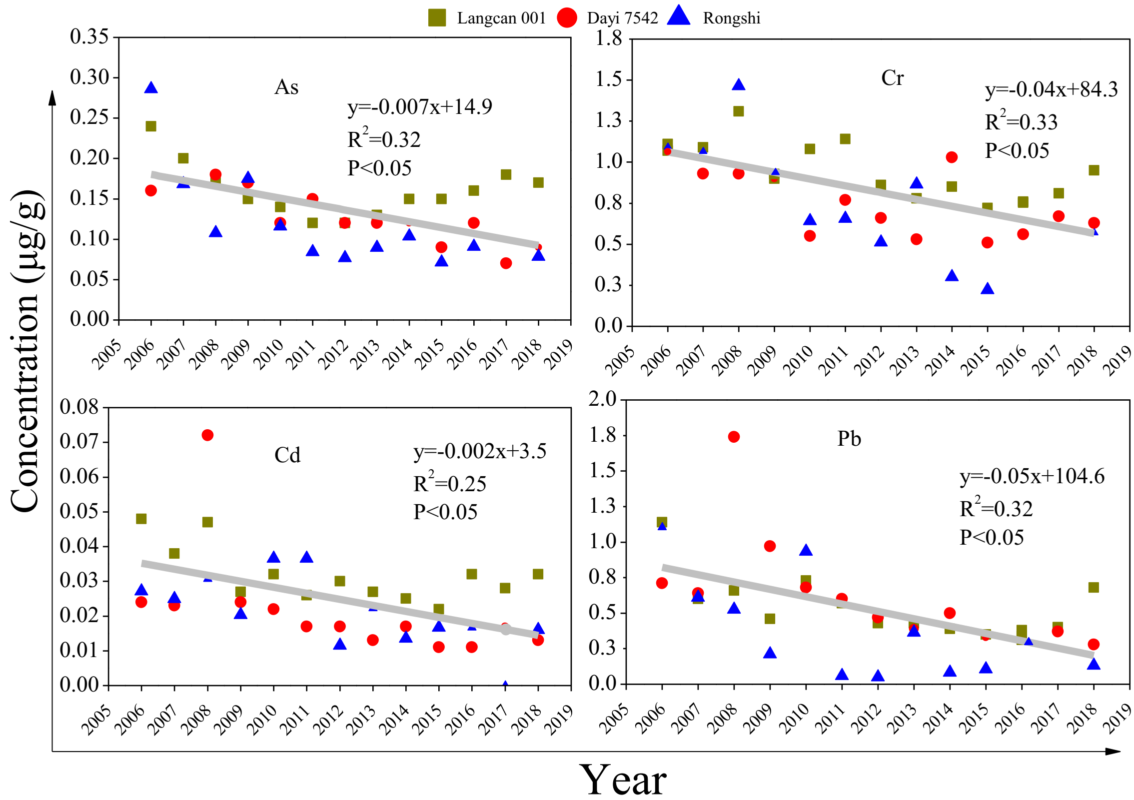

Fig. 2 Change trends of As, Cr, Cd, and Pb contents in raw Pu-erh tea with different storage years

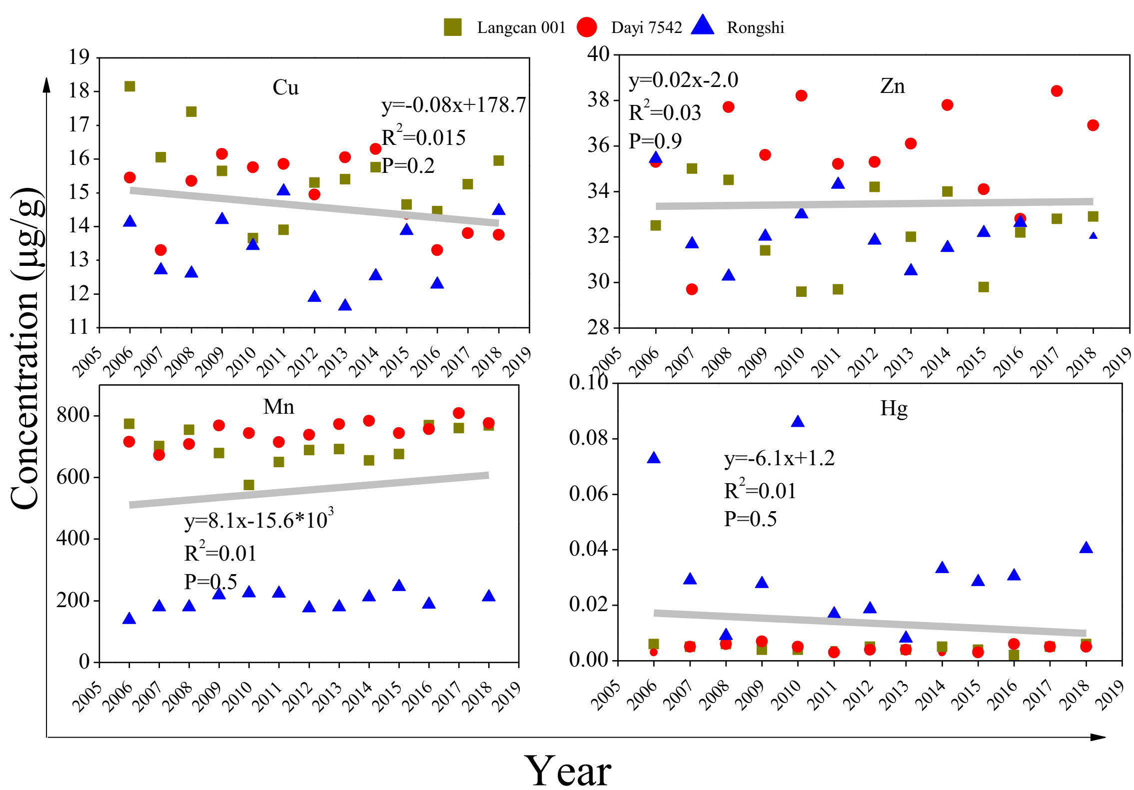

Fig. 3 Change trends of Cu, Zn, Mn, and Hg contents in raw Pu-erh tea with different storage years

Table 3 Descriptive statistics of microelement heavy metal content (μg/g) in raw Pu-erh tea with different storage years (n = 38)

Years	Number of samples (n)	As (μg/g)		Cr (μg/g)		Cd (μg/g)		Pb (μg/g)		Cu (μg/g)		Zn (μg/g)		Mn (μg/g)		Hg (μg/g)	
		Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD
2006	3	0.23	0.06	1.09	0.02	0.03	0.01	0.98	0.24	15.91	2.06	34.41	1.66	542.39	351.3	0.03	0.04
2007	3	0.18	0.02	1.03	0.09	0.03	0.01	0.62	0.02	14.02	1.78	32.13	2.68	517.53	293.03	0.01	0.01
2008	3	0.15	0.04	1.23	0.27	0.05	0.02	0.98	0.67	15.12	2.41	34.16	3.73	547.08	319.39	0.01	0
2009	3	0.17	0.01	0.91	0.02	0.02	0	0.55	0.39	15.33	1.01	33	2.27	555.06	295.12	0.01	0.01
2010	3	0.13	0.01	0.76	0.28	0.03	0.01	0.78	0.13	14.28	1.28	33.6	4.33	514.16	264.56	0.03	0.05
2011	3	0.12	0.03	0.86	0.25	0.03	0.01	0.41	0.3	14.93	0.98	33.07	2.95	529.17	266.64	0.01	0.01
2012	3	0.11	0.03	0.68	0.17	0.02	0.01	0.32	0.23	14.05	1.88	33.78	1.76	534.45	311.1	0.01	0.01
2013	3	0.11	0.02	0.73	0.17	0.02	0.01	0.39	0.03	14.36	2.39	32.87	2.9	547.99	322.14	0.01	0
2014	3	0.12	0.02	0.73	0.38	0.02	0.01	0.32	0.22	14.86	2.04	34.44	3.16	549.75	300.05	0.01	0.02
2015	3	0.1	0.04	0.48	0.25	0.02	0.01	0.26	0.14	14.28	0.39	32.03	2.15	554.49	270.57	0.01	0.01
2016	3	0.12	0.03	0.69	0.11	0.02	0.01	0.34	0.03	13.34	1.09	32.54	0.31	571.01	331.73	0.01	0.02
2017	2	0.13	0.08	0.74	0.1	0.02	0.01	0.39	0.02	14.53	1.03	35.6	3.96	784	33.94	0.01	0
2018	3	0.11	0.05	0.72	0.2	0.02	0.01	0.36	0.28	14.72	1.12	33.94	2.6	585.18	323.61	0.02	0.02
Mean		0.14	0.03	0.82	0.18	0.02	0.01	0.52	0.21	14.59	1.5	33.51	2.65	564.02	283.32	0.01	0.02
Min		0.1		0.48		0.02		0.26		14.34		32.03		517.53		0.01	
Max		0.23		1.23		0.05		0.98		15.91		34.41		784		0.03	

elements. To further identify the sources of heavy metals in tea, correlation analysis was conducted on 51 trace metal elements for 38 tea samples; then, the study data is processed by principal component analysis (PCA), and finally, the source of the data elements was identified. As shown in Fig. 4, three principal factors were obtained by PCA, which account for 75.7% of the variables of the study data, and three principal factors represented the geochemical combinations of different elements. The correlation of the element in this study was shown to have a significant positive correlation ($r > 0.7$, $p <$

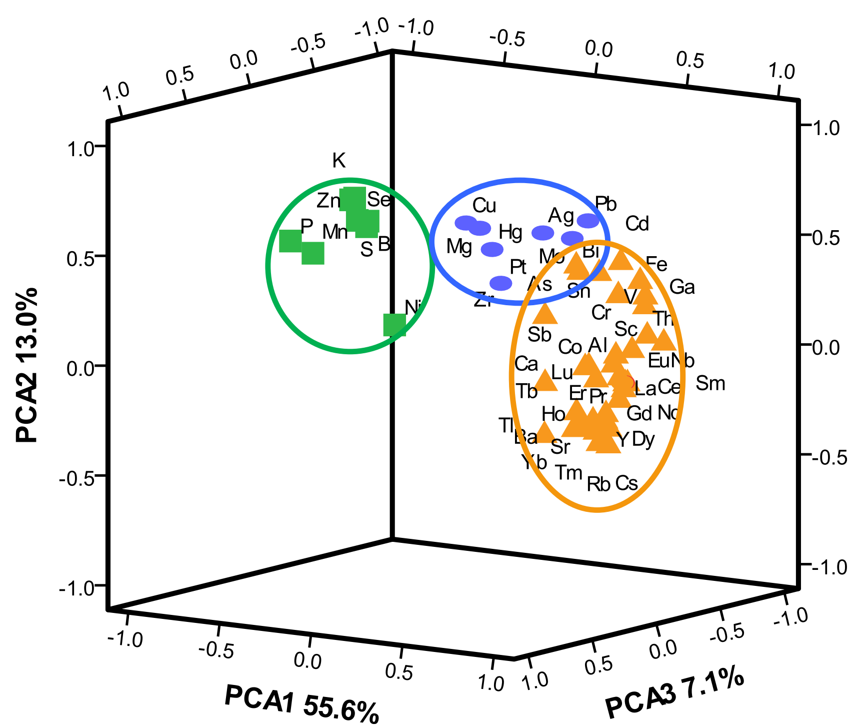

Fig. 4 Contribution rate of principal component factors by PCA

0.05) between the concentrations of the studied heavy metals. The correlation of element concentration of As/Cr (0.772), As/Pb (0.755), Cr/Cd (0.865), Cr/Pb (0.848), and Cd/Pb (0.884). As/Cd (0.52), As/Cu (0.576), Cr/Cu (0.558), Pb/Cu (0.544), Pb/Hg (0.490), and Zn/Mn (0.606) were found to have a moderate significant positive correlation ($r = 0.4$~0.7). However, in other pair elements of heavy metals, the values are less than 0.4.

The main factor 1 has high load values of Cr, Cd, As, V, Th, Sb, Co, Lu, Eu, Tb, Sm, Ho, Nd, Sr, Rb, etc. elements. The main factor 2 has high load values of Cu, Hg, Pb, Ag, and Mg elements. The main factor 3 has high load values of Zn, Mn, P, K, Se, S, and Ni elements. It was speculated that the heavy metal elements Cr, Cd, and As and rare-earth elements Th, Sb, Tb, etc. are from the same source. And the heavy metals of Zn and Mn and rare-earth elements Ni, Se, etc. are from the same source. However, studies have shown that Th, Sb, Lu, Eu, Ni, and Se are trace elements contained in geology [62]. Therefore, combined with the correlation analysis, it is speculated that both main factors 1 and 3 reflect the source of heavy metals as geological genesis, representing the geological origin of heavy metals in tea leaves. The main factor 2 has high load values of Cu, Hg, and Pb elements. As a global pollutant, atmospheric Hg can be transported for a long distance into remote ecosystem [63, 64]. Therefore, it was speculated that Cu, Hg, and Pb are from the atmosphere. Finally, Cu, Hg, and Pb in F2 (13.0%) may indicate that these elements come from the atmosphere, while Zn and Mn in F3 (7.1%) and Cr, Cd, and As in F1 (55.6%) may indicate that they come from soil.

Health Risk Assessment

Risk of Individual Metal by Consuming Raw Pu-erh Tea with Different Storage Years

Table 4 shows the values of EDIs of microelement heavy metals through drinking tea by adults. The order of average EDI values under various storage years of Pu-erh tea leaves was as follows: Mn > Zn > Cu > Cr > Pb>As>Hg>Cd. In this study, the EDI values of As, Cr, Cd, Pb, Cu, Mn, Hg, and Zn in tea samples' mean were 4.33×10^{-6}, 6.6×10^{-5}, 3.28×10^{-7}, 1.99×10^{-5}, 8.00×10^{-4}, 1.23×10^{-3}, 2.46×10^{-2}, and 1.23×10^{-6} (mg/kg bw/day), respectively. The EDI values of all heavy metal elements are less than RfD, indicating that there was no health or safety risk to consumers in consuming the studied Pu-erh tea product.

THQ was used to evaluate the human health risk. Table 4 shows the THQ values of heavy metals via drinking Pu-erh tea. In this study, for individual heavy metals, THQ < 1, which make clear the daily amount intake of each heavy metal may there is no potential health safety hazard to tea drinkers. Such results were consistent with the previous reports [14, 31, 33, 35, 65]. The THQ values of all heavy metal elements are in the order of Mn > Cu > As > Hg > Pb > Zn > Cd > Cr. Similarly, Zhang et al. have assessed the human health risk of tea from Guizhou Province and reported that the THQ values of each heavy metal element were all less than 1 and the order was as follows: Mn > Ni > Cu > Hg > As > Al > Zn > Pb > Cd > Cr [33].

Moreover, as shown in Fig. 5, there was no significant correlation between the THQ values of heavy metal elements (As, Cr, Cd, Pb, Cu, Zn, Mn, and Hg) in raw Pu-erh tea samples and storage years; the correlation coefficients (R^2) were 0.54, 0.57, 0.48, 0.59, 0.14, 0.07, 0.24, and 0.01, respectively. The result showed that the storage years showed no effect on the exposure risk of heavy metals (Table 5).

Combined Risk of Multiple Metals by Consuming Raw Pu-erh Tea with Different Storage Years

Table 4 shows the HI values of eight heavy metal elements from drinking Pu-erh tea. In this study, the HI values of all heavy metal elements were less than 1, indicating there is no health or safety risk from drinking of the Pu-erh tea from the brand, and there was no significant correlation of HI with storage years. Our results are comparable with previous results [31, 33]. However, in

Table 4 The results of correlation analysis of metal to metal in tea samples ($r = 95\%$)

	As	Cr	Cd	Pb	Cu	Zn	Mn	Hg
As	1							
Cr	0.772[a]	1						
Cd	0.52[a]	0.865[a]	1					
Pb	0.755[a]	0.848[a]	0.884[a]	1				
Cu	0.576[a]	0.558[a]	0.421	0.544[a]	1			
Zn	0.099	0.203	0.074	0.222	0.445	1		
Mn	− 0.161	− 0.191	− 0.39	− 0.254	− 0.028	0.606a	1	
Hg	0.41	0.097	0.198	0.49[a]	0.216	0.045	− 0.363	1

[a] Showing $p < 0.05$ (two-tailed)

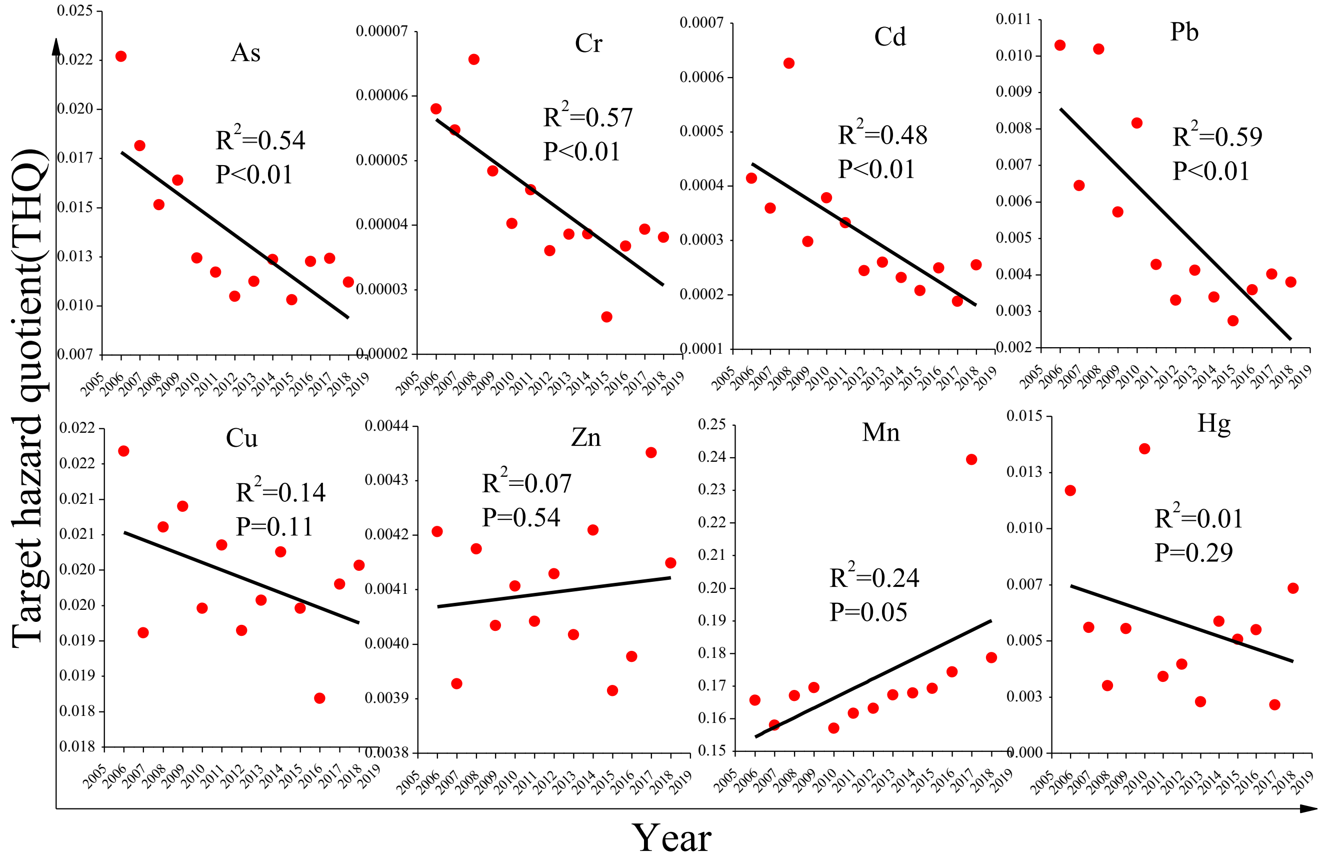

Fig. 5 Change trends of target hazard quotient (THQ) of As, Cr, Cd, Pb, Cu, Zn, Mn, and Hg for adults by drinking raw Pu-erh tea with different storage years

the present health risk assessment, there were some uncertain factors. Only the risks from 8 metal elements (Cd, Cr, As, Pb, Mn, Cu, Hg, and Zn) were taken into consideration through drinking tea, without considering the

Table 5 Estimated daily intakes (EDIs) (mg/kg bw/day), target hazard quotient (THQ), and hazard index (HI) values of microelement heavy metals for adults by drinking raw Pu-erh tea with different storage years

	Estimated daily intakes (EDIs)								Target hazard quotient (THQ)								
Years	As × 10^{-6}	Cr × 10^{-5}	Cd × 10^{-7}	Pb × 10^{-5}	Cu × 10^{-4}	Zn × 10^{-3}	Mn × 10^{-2}	Hg × 10^{-6}	As × 10^{-2}	Cr × 10^{-5}	Cd × 10^{-4}	Pb × 10^{-3}	Cu × 10^{-2}	Zn × 10^{-3}	Mn × 10^{-1}	Hg × 10^{-3}	Hazard index (HI)
2006	7.04	8.7	4.14	3.71	8.67	1.26	2.32	2.34	2.27	5.8	4.14	10.3	2.17	4.21	1.66	11.7	0.237
2007	5.63	8.2	3.59	2.32	7.64	1.18	2.21	1.12	1.82	5.47	3.59	0.64	1.91	3.93	1.58	5.59	0.212
2008	4.69	9.9	6.26	3.67	8.24	1.25	2.34	0.6	1.51	6.57	6.26	10.2	2.06	4.18	1.67	3.01	0.221
2009	5.08	7.3	2.98	2.06	8.36	1.21	2.37	1.11	1.64	4.84	2.98	5.72	2.09	4.03	1.69	5.54	0.222
2010	3.86	6.0	3.78	2.94	7.78	1.23	2.2	2.71	1.24	4.03	3.78	8.16	1.95	4.12	1.57	13.6	0.215
2011	3.63	6.8	3.32	1.54	8.14	1.21	2.26	0.68	1.17	4.55	3.32	4.28	2.04	4.04	1.62	3.41	0.206
2012	3.25	5.4	2.45	1.19	7.66	1.24	2.28	0.79	1.05	3.6	2.45	3.3	1.91	4.13	1.63	3.96	0.205
2013	3.48	5.8	2.6	1.49	7.83	1.21	2.34	0.46	1.12	3.86	2.6	4.13	1.96	4.02	1.67	2.29	0.209
2014	3.83	5.8	2.32	1.22	8.1	1.26	2.35	1.18	1.24	3.87	2.32	3.39	2.03	4.21	1.68	5.88	0.214
2015	3.20	3.9	2.08	0.98	7.78	1.17	2.37	1.01	1.03	2.57	2.08	2.73	1.95	3.92	1.69	5.06	0.211
2016	3.80	5.5	2.49	1.29	7.28	1.19	2.44	1.1	1.23	3.68	2.49	3.59	1.82	3.98	1.74	5.5	0.218
2017	3.85	5.9	1.88	1.45	7.92	1.31	3.35	0.43	1.24	3.94	1.88	4.02	1.98	4.35	2.39	2.15	0.282
2018	3.47	5.7	2.55	1.37	8.03	1.25	2.5	1.47	1.12	3.81	2.55	3.8	2.01	4.15	1.79	7.34	0.226
Mean	4.33	6.6	3.28	1.99	8.00	1.23	2.46	1.23	1.36	4.35	3.11	5.39	1.99	4.1	1.72	5.77	0.221

influence of other exposure ways on the health risk, such as food, breathing, skin contact, and other harmful elements (such as antimony, tin, cobalt, thallium, iron, and rare-earth elements), which underestimated the risk of heavy metals. Moreover, in the calculation of exposure dose, the occurrence forms of metal elements were not considered, and the total exposure dose was calculated directly, so that the evaluation results were higher. Therefore, there may be some deviations between the final health risk value and the real value in the present study. More research is needed to assess health risk by consumption of Pu-erh tea.

Conclusion

In our study, the heavy metal As, Cr, Cd, Pb, Cu, Zn, Mn, and Hg concentrations in raw Pu-erh tea with different storage years ranged 0.10~0.23, 0.48~1.23, 0.02~0.05, 0.26~0.98, 14.34~15.91, 32.03~34.41, 517.53~784.00, and 0.01~0.03 μg/g, respectively, and all heavy metal element concentrations were below the threshold of relative standard values for tea products. These results indicate the quite good quality of tea leaves in Pu-erh. Furthermore, the mean values of THQ and HI of Pu-erh tea products were below 1, which represents the consumption of infusions of raw Pu-erh tea with different storage years would not pose health risks of heavy metal elements to a normal adult.

Moreover, there was no significant correlation between heavy metal element (As, Cr, Cd, Pb, Cu, Zn, Mn, and Hg) contents in raw Pu-erh tea samples and storage years. The correlation coefficients (R^2) range from 0.01 to 0.33. Furthermore, there was no significant correlation between the THQ values of heavy metal elements (As, Cr, Cd, Pb, Cu, Zn, Mn, and Hg) in raw Pu-erh tea samples and storage years; the correlation coefficients (R^2) range from 0.01 to 0.57. The result showed that the storage years showed no effect on the exposure risk of heavy metals. The heavy metal elements in tea samples come from the atmosphere and soil. The elements Cu, Hg, and Pb may come from the atmosphere, while Zn, Mn, Cr, Cd, and As may come from soil.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

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