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Geological load and health risk of heavy metals uptake by tea from soil: What are the significant influencing factors?

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ABSTRACT

As one of the most popular beverages around world, factors influencing transfer of heavy metals from soil to tea leaves is crucial to investigate and assess health risk through tea drinking. Parent material (PM), soil and tea samples from Anhui province, typical tea producing area in China were collected in this study. To find out distribution characteristics of heavy metals in tea and soil, and influencing factors for transfer process, variables of plantation factors, soil properties and geological background were taken into account. The results showed that weathering pedogenic process could be the main release source of heavy metals in soil under the acid environment for tea growth. More than 75% of soil Cd, Hg, Pb and Zn exceeded background. However heavy metals in tea samples were below the limits of China, WHO and EU standards. Soil organic matter and redox process influenced the distribution and transfer of As, Pb, Cd and Hg in soil and tea. While geochemical behaviours of Cr, Cu, Ni and Zn were mainly related to soil pH and iron oxides in tea garden. The method of classification and regression trees (CART) showed clones of tea type, bedrock type, soil texture, soil organic and fertilizer application were identified as the main factors influencing transfer factors of heavy metals from soil to tea. The specific types of tea grown in the soil with sandy clay and bedrock of granite/granodiorite and shale should be given more monitoring. The non-carcinogenic hazard quotients (HQ) and cancer risk (Risk) through tea drinking were primarily caused by Pb and Cd respectively. To reduce the potential health risk from tea, application of organic and/or compound fertilizer were thought to be the effective management strategy for tea plantation.

1. Introduction

Tea (*Camellia sinensis L*), as the plant for one of the most popular hot beverages, is cultivated over 45 countries around the world, especially in Asia (Jain, 1999). According to historical records, tea has been cultivated in China for over 2000 years (Mondal, 2009). Besides differences in the manufacturing process, specific tea cultivars are used to produce various types of tea, such as green tea, oolong tea, black tea, jasmine tea and so on (Baruwā, 1989; Mondal, 2009). Due to its reduction effect on serum cholesterol and lipoprotein oxidation by its antioxidant activity, drinking tea could help to decrease the risk of diabetes, cardiovascular disease and cancer (Cabrera et al., 2003; Chung et al., 2003; Kono et al., 1992). So different tea types are popularly consumed around the world, especially in Asia. Apart from the benefits derived from the organic chemical composition such as polyphenols, theogallin, amino acid theanine, many trace elements such as Al and Mn accumulate in tea (Karak and Bhagat, 2010; Reto et al., 2007).

Given concerns about the potential adverse effect of Al, many research reports are focused on Al and F in tea and tea infusion before (Karak and Bhagat, 2010; Salahinejad and Aflaki, 2010). However, other heavy metals in tea could cause accumulative chronic and acute human health issues through oral pathway (Hosseini Koupaie and Eskicioglu, 2015; Lu et al., 2015). Therefore, as one of the most popular beverages, heavy metals in tea are attracting attention gradually (Schmite et al.,

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2019; Yemane et al., 2008; Zhang et al., 2020). The presence of heavy metals in tea infusion could exceed the daily permit in some countries (Karak and Bhagat, 2010). To manage the safety of tea plantation and monitor tea production, a lot of research focused on the uptake and accumulation of heavy metals in tea leaves or tea infusion is critical (Karak and Bhagat, 2010; Salahinejad and Aflaki, 2010). The infusion rate of different heavy metals vary between ~10%- ~60%, with about 90% of heavy metal infusing into the gastro-intestinal system (Karak and Bhagat, 2010; Malik et al., 2008; Schmite et al., 2019; Schulzki et al., 2017). Yet studies about how and what characteristics of heavy metals promote entry into the tea plant are rarely reported.

It is well-known that economic development and human activities are responsible for serious environmental issues caused by heavy metal accumulation in agricultural system around world (Li et al., 2014; Lu et al., 2015). Anthropogenic sources caused by human activities, such as traffic, fertilizer application, industry and mine exploration could release heavy metals into soil (Qiang et al., 2016). Unlike most of traditional crop plants, because of it need for good drainage, tea plants prefer growing in hills or mountainous regions which are often far away from cities or towns (Baruwā, 1989; Mondal, 2009). So geological background and natural factors are the main sources of heavy metals in tea (Huang et al., 2019; Zhang et al., 2020). From previously published research reports, it is evident that relatively high heavy metals could easily be observed in soil from sedimentary backgrounds or parental bedrocks such as sedimentary rocks, shales or carbonates (Vandecasteele et al., 2005; Zhang et al., 2020). Enrichment of soil heavy metals from these environments were related to depositing and burying of organic matter (Starr et al., 2003). But in fact, due to heterogeneous distribution of trace elements in the same type of rock, heavy metals concentrations in soil could be different with same parental bedrock (Anda, 2012; Hu and Gao, 2008). This could make influence of soil types on heavy metal in crop plants insignificant or "invisible", although there are significant differences in heavy metal concentrations in different soil types in some cases (Kawada et al., 2002; Yang et al., 2014).

Beside minerals properties, soil pH is thought as the main factor that influence the transfer and accumulation of heavy metals from soil to crop plant (Kabata-Pendias and Pendias, 2001). Tea plant prefers growing in areas with good drainage and acid soil, particularly in subtropical and tropical regions (Baruwā, 1989). Appropriate soil pH for the growth of tea plant varies between ~4 and 6.5 (Baruwā, 1989). So tea plant have higher potential risk of heavy metal accumulation from soil under low soil pH (Fung and Wong, 2002). Previous researches have focused on the accumulation and toxic risk of Al and F in tea leaves because of their enrichment with these elements (Fung et al., 2003). Apart from the abnormal enrichment of Al, Mg and Mn, tea plant also accumulates heavy metals such as Zn, Cu and Ni easily (de Oliveira et al., 2018; Malik et al., 2008). Thus Zn, Cu and Ni levels in tea could reach 2 to dozens of times higher than As, Cd, Hg levels (Karak and Bhagat, 2010). A comparison showed that As, Cd, Cu, Cr and Pb in green tea were ~1–5 times lower than those in black tea, in most cases (Karak and Bhagat, 2010). Various concentrations of metals in the same and different clones of tea plants indicated that accumulation process of heavy metals of tea from soil pool could be influenced by both tea plant metabolism and heavy metals concentration in soil directly under acid soil condition (Chen et al., 2009; Yemane et al., 2008). Geochemical behavior of elements in soil-plant system including active translocation and passive transfer by plants metabolism has been proved (Fodor, 2002; Kabata-Pendias and Pendias, 2001). Geological background and acid soil condition supply plenty of labile elements. Some special geological strata and rocks such as limestone have been observed to influence the accumulation of heavy metals in tea plant (Zhang et al., 2020). Status differences of heavy metals concentrations between clones of teas, plantation years, bedrocks, soil properties and other natural factors have been investigated and tested. However, the factor that could preferentially influence transfer of specific heavy metals and the characteristics of metals during mobilization soil to tea plant are still unknown.

Statistical data from the United Nations suggest that the average tea production per year in China (>2 million tons) occupies ~35–40% of total production of world in the most recent 10 years (FAOSTAT, 2020). In China, over 80% of tea production and consumption are related to green tea (National Bureau of Statistics of China, 2020). Therefore, it is important to investigate the transfer and accumulation of heavy metals in green tea from soil to tea plant. This study aims at exploring the factor influencing transfer and accumulation characteristics of heavy metals from soil to tea plant. In the latest researches in this field, stochastic statistic method such as classification and regression trees (CART), has been used to identify the distribution or source of heavy metals in soil (Hu and Cheng, 2013; Wu et al., 2020; Zhong et al., 2014). One of the attractions of this method could fully consider numerical and non-numeric variables without further assumptions before it is applied. Therefore, the object of this study was to screen the main factors for influence distribution and transfer of heavy metals in soil and tea. Principal component analysis (PCA) and non-parameter test were applied to discuss distribution characteristics of heavy in soil and tea under different conditions of plantation factors, soil properties and geological background. Furthermore, by using CART method, the order of importance for various factors influencing transfer of heavy metals from soil to tea will be distinguished according to bedrock type, parent material, soil properties, clone of tea type and etc. The transfer and accumulation of metals from soil to tea could thus be modelled and characterized. While the potential health risk of tea to heavy metals caused by geological background could also be evaluated and compared with transfer characteristics of heavy metal. The results of this work could supply a new thought on how the geological condition and soil properties influenced health risk caused by heavy metals in tea and assist the formulation of agricultural management for tea gardening.

2. Materials and methods

2.1. Study area and sampling

The study area is located in the mountainous region of Southern Anhui province, China. This region represents a typical area of green tea production in China, and is located in the subtropical zone with ~1100 mm of average annual precipitation and ~5- ~25 °C of average daily temperature. A total of 85 sampling sites were selected from 4 traditional tea areas in Anhui province, China (Fig. 1). In each area, one clone of green tea was chosen. Type 1 tea samples with thick stems, large leaves and thick leaf skins, were collected from Shitai. The type 2 tea samples from Jingde have straight and flat leaves and fat buds with green and white hair. Type 3 tea samples from Jingxian are similar to type 2, but have more plump buds. The color of type 3 tea is greener than that of type 2. The buds and leaves of type 4 growing in Yuexi are connected, which stretch like a small orchid. The color of type 4 is the same as that of type 3. The corresponding information about sampling environment and samples was recorded for each site, including plantation factors (clones of tea type, fertilizer application, type of land use and plantation year), soil properties (soil pH, organic carbon and etc.) and geological background (type of parent material, bedrock type, and terrain environment) (Table S1).

Geographically, the type 1, 2, and 3 are located in Yangtze Para-platform while area of type 4 is in the Dabie Mountains. The geological strata in type 1 area are Silurian (S) with large-area outcroppings of intrusive granite and other acid rock (γ_5), Devonian-Triassic (D-T), Nanhua Period (Nh) with sandstone and shale, Sinian (Z) with siliceous rock, Cambrian (Є) with shale and Ordovician (O) with shale mainly (Fig. 1). In type 2 area, Silurian (S), Cambrian (Є) and Ordovician (O) are predominant, with granite/granodiorite, limestone and sandstone mainly. Type 3 samples are distributed in the area with Silurian (S) Tangjiawu formation, and located in Devonian (D) and Carboniferous-Permian (C-P) sporadically. The lithology is sandstone/quartz

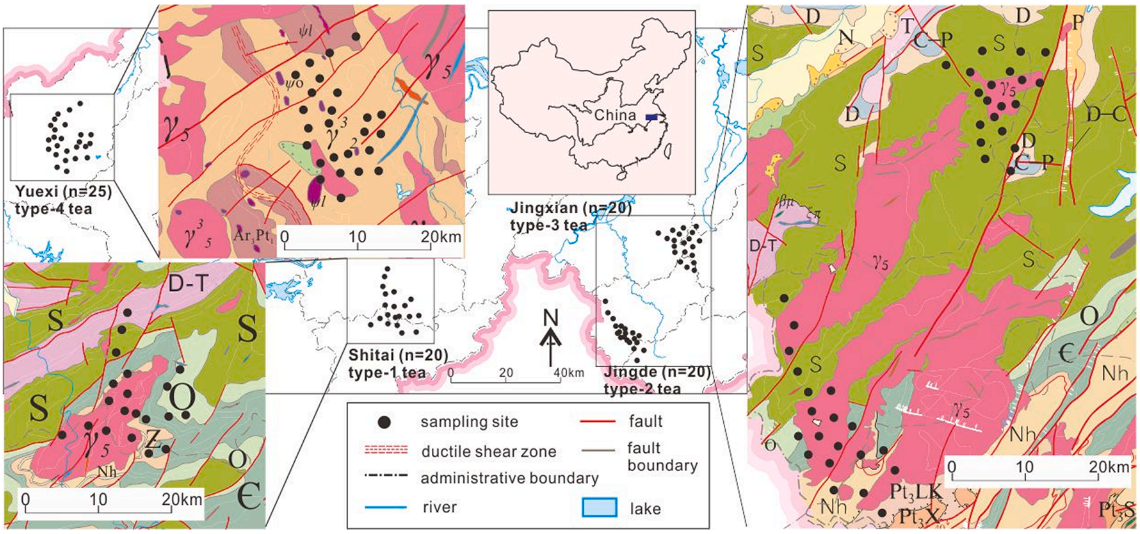

Fig. 1. The location and geological background of 85 sampling sites in South Anhui, China.

sandstone and granodiorite. Type 4 samples were mainly collected from Proterozoic stratum (Ar_3Pt_1) in Dabie Mountains, with metamorphic intrusive rock series including granite and granodiorite, and sporadic tuffite.

Systematic sampling scheme was designed and applied in 4 areas, including tea leaves, soil, weathering parent material in. Each site has an area of about 100 × 100 m from where four subsamples were collected randomly and mixed to obtain a bulk sample for tea leave, soil and weathering parent material (PM). The green tea samples were collected and sealed in plastic bags and taken back to the laboratory. Fresh tea leaves samples were weight first. Then, they were twice cleaned with distilled water to remove dust and impurities. Cleaned tea leaves samples were dried in an oven below 50 °C to a constant weight for the further chemical analysis. The ratios of the weights of dry samples to fresh tea samples were calculated to calibrate the results of heavy metals in fresh tea.

The soil samples were collected from tea gardens at a depth of 0–20 cm from the top soil layer. Plastic shovels were used to collect the soil in each tea sampling site to avoid contamination from metal impurities. Then stones and other debris were picked out. Four soil samples were collected and mixed into one bulk sample. The collected soil samples were stored in plastic bags and taken to the laboratory to store at room temperature (~25 °C). Each soil sample was air-dried and ground to <2 mm for further test, including pH, chemical analysis and etc. While at each site, a ring sampler with volume of 100 cm^3 was used to insert horizontally into the soil. Then the ring sampler full with fresh soil sample was put into one plastic bag for soil bulk density test. Before sampling, each ring sampler was washed and dried to weight at lab. The ring samplers with soil were weight at balance in the lab as soon as samples collection finishing. Meanwhile, a part of soil sample in the ring sampler was taken to test the soil moisture. The soil bulk density was calculated using the difference between weights of ring samplers before and after sampling, volume and soil moisture. The whole procedure of soil bulk density was carried out following the Soil Testing-Part 4: Method for Determination of soil bulk density (NY/T 1121.4–2006).

The weathering parent material (PM) samples were collected from an appropriate soil profile "C" layer with a depth of ~60 - ~200 cm, near to the tea leave and soil sampling site. The parent material sample is mixture of soil minerals such as clay, Fe and Mn oxides/hydroxides, and small rock debris. The samples were stored in plastic bags and taken to the laboratory to store at room temperature (~25 °C). Each parent material sample was treated as soil samples, being air-dried and ground to <2 mm for further chemical analysis.

2.2. Chemical analysis

2.2.1. Tea

The dried tea leave samples were milled before chemical analysis. About 1 g (dry weight) of milled tea leave sample was put into Teflon tubes. The samples were digested using mixed acid solution of 10 ml HCl (ρ = 1.19 g/ml), 10 ml HNO_3 (ρ = 1.42 g/ml), and 10 ml $HClO_4$ (ρ = 1.68 g/ml) in vessels at 180 °C in a microwave oven (ETHOS TOUCH CONTROL, Milestone Inc., Italy). All acid solutions were distilled before digestion. The digested samples were subsequently diluted to 50 ml with deionized water (18.2 MΩ) from a MilliQ system (Millipore Corp., USA) prior to the chemical analysis.

2.2.2. Soil and parent material

Dried soil and weathering parent material samples were ground further, then passed through a 100-mesh sieve. After being ground and sieved, small quantities (~1.0 g dry weight) of dried soil samples was dissolved with mixed acid of concentrated HCl, HNO_3, $HClO_4$ and HF. Samples were digested at 180 °C in a microwave oven (ETHOS TOUCH CONTROL, Milestone Inc., Italy). The digested solutions were diluted with MilliQ water prior to the chemical analysis. Soil organic matter was expressed using soil organic carbon (C_{org}) which was analyzed in the Vario MACRO CHN analyzer (Elementar, Germany) at 850 °C. Before analyzing at instrument, soil samples were digested with 1 mol/L HCl to remove the carbonates. And the residue was washed using MilliQ water and dried for C_{org} measurement.

For tea leaves, soil and parent material samples, Cd, Cr, Cu, Ni, Pb and Zn, Fe and Mn in diluted solution were determined by inductively coupled plasma mass spectrometry (ICP-MS X SERIES, Thermo Fisher Scientific, USA). As and Hg were measured on cold vapour atmospheric fluorescence spectrometry, AFS 230E (XGY-1011A, IGGE, China). The concentrations of heavy metals in tea, soil and parent material samples were calculated and expressed as mg/kg for the dry weight of each solid sample.

For chemical analysis, quality assurance and quality control (QA/QC) protocol were followed to ensure the reliability and precision of results. High-quality deionized water was used for rinsing glassware, preparation of standards and dilution of samples. Reagent blanks were analyzed, and the data were subsequently blank-corrected to remove analytical error. To ensure the reliability of results, standards (GSS-2, 4, 6) of the respective metals were run after every ten samples analyzed. And relative standard deviation (RSD) of replicate measurements were <5%.

2.3. Method of health risk assessment

The health exposure risk assessment method proposed by the US EPA was applied (US EPA, 1989; US EPA, 2011). This method evaluates human health exposure risk through three main pathways, dermal exposure, respiratory system and oral ingestion. Health risk from tea drinking is caused through oral ingestion pathway. To evaluate this at the maximum level, a hypothesis of 100% infusion rate of heavy metals in tea was proposed in this study.

From US EPA protocol of human health risk assessment, all assessment indexes were based on the average daily intake (ADI) (mg/kg-day) calculation by Eq. (1):

$$ADI = \frac{C \times IR \times EF \times ED}{BW \times AT} \tag{1}$$

where C is the specific metal concentration in tea leaves (mg/kg); IR is the ingestion rate of tea drinking, converted to consumption of tea leaves (kg/day), which was selected as 11.4 g/day (Peng et al., 2018); EF represents the exposure frequency, and is assumed to be 365 day/per year; ED is the exposure duration (year), assumed as 57 years (according to local and US surveys (Mitchell et al., 2014), the age of people drinking tea regularly is above 15 with an average life span of 72 years); AT is the time period (day), can be calculated as: AT = ED × 365 day; BW is the body weight of the exposed people with 61.75 kg for adults (NHFPC (National Health and Family Planning Commission), 2015). The non-carcinogenic risk for a specific metal in tea was evaluated by the hazard quotient (HQ) calculated by Eq. (2), and total non-carcinogenic risk for multiple metals (THQ) was sum of all HQ values for heavy metals, following Eq. (3):

$$HQ_i = ADI_i / RfD_i \tag{2}$$

$$THQ = \sum_{i=1}^{n} HQ_i \tag{3}$$

where RfD_i is the reference oral dose (mg/kg·day) of a specific metal i. US EPA Integrated Risk Information System (IRIS) gives values for As (0.0003), Cd (0.001), Cu (0.04), Cr (1.5), Zn (0.3) (US EPA, 2016). RfD value for Hg (0.00016) was calculated by US EPA. Reference dose of Pb was selected as 0.00014 mg/kg·day from Oak Ridge National Laboratory, US (Qu et al., 2012). According to criteria from US EPA, if the HQ and/or THQ are above 1, it is thought that the exposed people could experience adverse health effects. If HQ and/or THQ are less than one, the heavy metal concentrations in tea is thought to be safe for human health (US EPA, 1989).

The carcinogenic risk is evaluated using cancer slope factor (SF). The risk caused by a specific metal can be calculated by Eq. (4), and the total risk is the sum of the risks of all heavy metals calculated using Eq. (5):

$$Risk_i = ADI_i \times SF_i \tag{4}$$

$$Risk_{total} = \sum\nolimits_{i=1}^{n} Risk_i \tag{5}$$

where $Risk_i$ is the health risk of a specific carcinogenic metal i. The cancer slope factor SF (kg·day/mg) was selected as 1.5 for As and 0.5 for Cr, according to US EPA Integrated Risk Information System (IRIS), 0.0085 for Pb and 15 for Cd from California OEHHA Toxicity Criteria Database (Zhang et al., 2015). The $Risk_{total}$ is the sum of $Risk_i$ values of all metals. The carcinogenic risk for $Risk_i$ or $Risk_{total}$ is classified as: no significant risk ($<10^{-6}$); acceptable/tolerable (10^{-6} to 10^{-4}); or unacceptable ($>10^{-4}$) (US EPA, 2001).

2.4. Statistical analysis

Transfer factor (TF) was introduced to characterize the transfer process of heavy metal from soil to tea leaves, which has been applied in the researches about rice and wheat successfully (Mao et al., 2019; Williams et al., 2007). The TF values were calculated by contents of specific metal in tea leaves sample and soil sample, following the Eq. (6) as blow:

$$TF_i = C_{tea} / C_{soil} \tag{6}$$

where TF_i represent the transfer factor of specific metal "i"; C_{tea} and C_{soil} were concentration of metal "i" in tea leaves and soil samples.

Data statistical analysis, decision tree method with method of classification and regression trees (CART) and principal component analysis (PCA) with varimax rotation were performed by SPSS software package (SPSS Inc. Version 16, 2007). The definition of variables or factors using in CART and importance order of variables from CART are shown in supplementary information. The detailed explanation and calculation principle have been described and reported in study before (Hu and Cheng, 2013; Zhong et al., 2014). The non-parameter test for k independent samples (Kruskal-Wallis Test) were conducted to analyze the difference of distribution of heavy metals in tea and soil, using Origin software (OriginLab Corporation, version 8.5, 2010).

3. Results and discussion

3.1. Concentrations of heavy metals in tea leaves, soil and parent material

3.1.1. Parent material (PM)

The results of concentrations of heavy metals in tea leaves, soil and PM samples are shown in Table 1. As known well, weathering PM is primary origin of elements and minerals in soil due to pedogenic process (OERTEL, 1961). Without plenty of human activities, chemical properties such as heavy metals in soil are always released from PM weathering mainly (Starr et al., 2003). According to statistical baseline values of elements in soil layer "C" collected from the same study area (Chen et al., 2012), it can be seen that except As, other metals levels were the same as updated upper continental crust (UCC) (Hu and Gao, 2008). Unlike deep soil in Chen et al. (2012), the pH of PM collected in the tea garden was lower in this study (Table 1). This indicated that the tea cultivation could acidify the soil condition which tea plant prefer (Mondal, 2009). In comparison with UCC and background baseline values, all heavy metals in PM were higher than UCC and background values due to the lower pH (<6). Under this condition, Cd, Hg and Zn levels in more than 70% of samples were higher than the background baseline and/or UCC levels. As major elements, the contents of Fe and Mn in PM were same as the background values. But more organic carbon occurred in PM in this study. Generally, the enrichment of heavy metals in PM followed the order: Zn, Cd > Hg > Pb > As, Cu > Ni > Cr. As investigation in the field, granite, granodiorite and diorite are predominant, with sporadic distribution of sandstone, limestone, shale and other bedrock (Table S1). This could be the reason why the most weathering PM is acid and clastic material at lower pH (average pH 5.8). In the examination before, it has been concluded that although rough indication values of trace elements cannot be obtained from the original parent rock due to complex weathering and pedogenic processes, the levels of trace elements in soil were closely related to those in the parent material with the same soil profile (OERTEL, 1961).

3.1.2. Soil

The concentration of heavy metals in soil are shown in Table 1. The pH of soil samples in this study varied between 3.79 and 6.4 (average pH 5.00). According to the properties of surface soil in Yangtze-Huaihe River basin, soil from tea garden was more acid (Chen et al., 2012). This value was similar to the study in tea garden of Anhui Province (Peng et al., 2018). This could indicate long-term tea plantation would decrease the soil pH and release heavy metals (Zhang and Fang, 2007). And in the study in Guizhou, the soil pH in tea garden was much lower (Zhang et al., 2020). This meant that except tea planation, different

Table 1
Concentrations of heavy metals (mg/kg) in tea, soil and weathering parent material (PM), and main physio-chemical properties in soil and parent material (PM).

tea	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn				
min	0.013	0.007	0.046	0.833	0.001	0.465	0.062	4.646				
max	0.190	0.168	2.578	8.264	0.041	11.609	2.072	15.551				
mean	0.079	0.046	0.355	4.000	0.012	2.194	0.639	8.662				
StD	0.046	0.032	0.463	2.047	0.010	2.081	0.489	2.756				
China[a]	2.000	1.000	5.000	30.000	0.300		5.000					
WHO[b]	1.000	0.300					10.000					
EU[c]		1.000			0.100		3.000					
soil	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**	**Fe_2O_3(%)**	**Mn**	**C_{org}(%)**	**pH**
min	1.029	0.062	23.700	13.100	0.016	10.000	17.100	47.700	2.700	105.800	0.419	3.79
max	211.639	0.761	288.800	184.100	0.179	136.000	174.300	164.800	13.060	2256.800	6.850	6.40
mean	16.347	0.249	63.353	37.167	0.073	28.168	40.594	106.476	5.546	841.325	2.018	5.00
StD	30.685	0.165	52.612	27.964	0.041	23.125	25.213	27.486	2.253	429.013	1.157	0.58
China[d]	40	0.3	150	50	1.3	60	70	200				
background[e]	9.400	0.104	69.400	24.900	0.041	25.000	25.900	53.200	4.440	525.200	1.100	5.85
PM	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**	**Fe_2O_3(%)**	**Mn**	**C_{org}(%)**	**pH**
min	0.300	0.040	8.900	5.100	0.002	4.300	12.400	22.900	1.560	145.600	0.080	4.72
max	294.600	1.194	225.900	116.800	0.140	52.200	441.000	253.400	12.280	3368.400	3.920	8.31
mean	12.223	0.179	45.300	25.902	0.036	21.205	37.404	96.052	5.317	789.501	0.688	5.80
StD	34.098	0.201	33.652	22.538	0.028	13.675	49.059	39.196	2.133	476.848	0.743	0.69
background[f]	11.4	0.061	82.7	27.8	0.014	35.5	25	63.2	5.66	769.7	0.2	7.75
UCC[g]	5.7	0.06	73	27	–	34		75				

a. Standards for tea in China, including GB2672-2017, NY659-2003 and NY/T288-2012; **b.** limits for metals in herbal material from WHO (World Health Organization, 2007); **c.** maximum levels for metals in foodstuff by European Union (Commision of the European Communities, 2020); **d.** Soil environment quality Risk control standard for soil contamination of agricultural land for China (GB15618-2018) (Ministry of Ecology and Environment, 2018); **e.** and **f.** statistical background values for surface soil and baseline values from layer "C" of soil profile samples from data collected by Chen et al. (2012); **g.** trace elements content in the upper continental crust (UCC) updated by (Hu and Gao, 2008).

geological background could result in various soil condition during weathering and pedogenic process, such as pH, secondary mineral phase and so on. As shown in Table 1, in comparison with background value (Chen et al., 2012), soil organic matter doubled due to long-term agricultural activities, which could also induce decrease in the soil pH (Kabata-Pendias and Pendias, 2001; Yu et al., 2017). In acid condition, elements are easily released from soil. Besides little higher soil Fe and Mn, more than 75% of soil from tea garden exceeded the background values for Zn, Cd, Pb and Hg (Table 1). Similar to PM, the order of enrichment of heavy metals in soil followed: Zn > Cd > Pb > Hg > Cu > As, Ni > Cr. But according to soil quality standard of China (GB15618-2018) for dry soil with pH < 5.5, only about 20% of Cd and Cu were above limits (Ministry of Ecology and Environment, 2018). And soil Zn and Hg were at safe levels. The heavy metals in soil were slightly lower than those in the samples from tea gardens in the studies before (Peng et al., 2018; Zhang et al., 2020), which implied could be due to their geological backgrounds.

As field information about geological background in this area, acid and clastic material predominated in PM samples. While heavy metals contents in PM showed an exponentially decreasing relation with the ratio of heavy metals in soil to PM, which showed the possible accumulation of elements in soil from weathering PM during pedogenic process (Fig. 2). The average ratio of background values of soil to baseline values of PM for heavy metals followed the order: Hg > Cd > Pb > Cu, Cr, Zn, As, Ni (Chen et al., 2012). Likewise the mean values of ratio of heavy metals in soil to PM were As, Hg > Cd, Cu, Cr, Ni > Pb, Zn in this study. It can be deducted that the release and accumulation of Cd, Cu, Cr, Ni and Zn during weathering and pedogenic process in the study

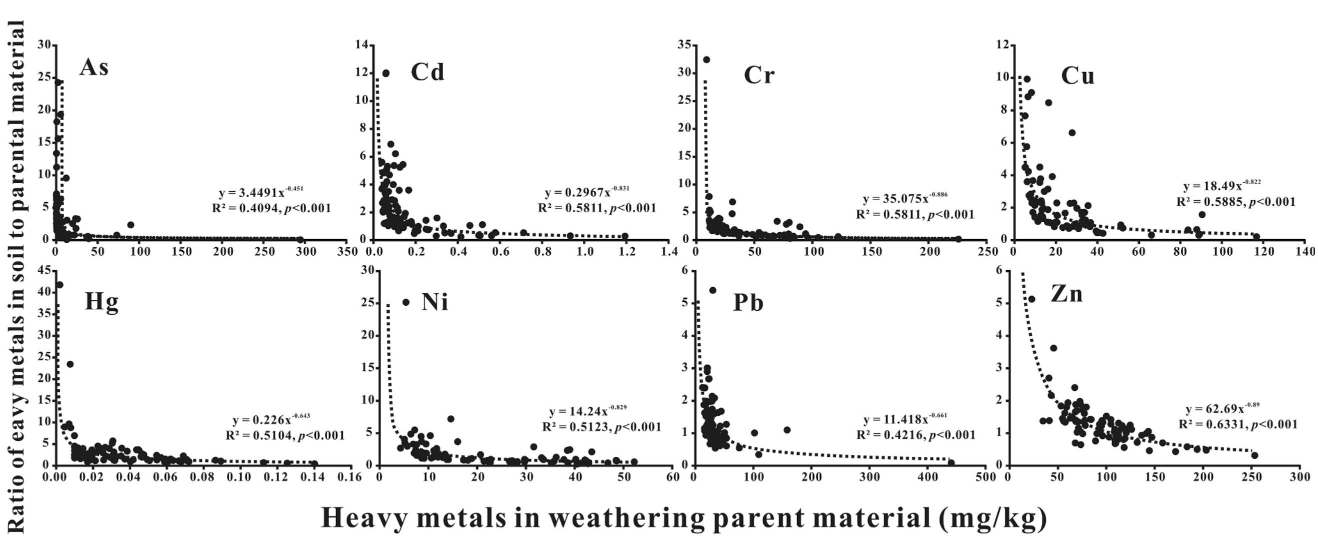

Fig. 2. Exponential correlation between increasing heavy metals level in weathering parent material and ratios of metal concentrations in soil and parent material samples.

area, even in the whole Yangtze River - Huaihe River basin were homogeneous. This could be the reason for the exponents of equations for Cd, Cr, Cu, Ni and Zn fell in −0.822- −0.89 in Fig. 2. While the exponents of equations for As, Hg and Pb could imply the different levels and release intensity in various bedrock under acid environment. Plenty of researches prove that weathering rates are different for various rocks and/or minerals (Hu and Gao, 2008; Wayne Nesbitt and Markovics, 1997). Commonly, carbonate and shale are considered to be the most weathered with the Chemical Index of Alteration (CIA) values of ~70-~90. And CIA values for granite and granodiorite varied between ~45 and ~75 (Meunier et al., 2013; Wayne Nesbitt and Markovics, 1997). In the study about weathering release of heavy metals from parent material and soil in Finland with granite/granodiorite bedrock, the average weathering rates were calculated and evaluated (Starr et al., 2003). According to the rates for specific heavy metals, it can be estimated that time of release of heavy metals were about 90–230 years for PM and about 120–260 years for soil. The study area locates in subtropical zone with abundant precipitation. It is reasonable for the actual weathering rates of heavy metals to be higher in this study than those in study in Finland, especially in acid soil environment. Thus, the time of release for heavy metals is possibly much lower than the values calculated, especially with lower pH condition. This means that heavy metals could accumulate in tea tree at high levels after decades of tea plantation.

3.1.3. Tea leaves

Heavy metals in all tea leave samples were below the standard limits of China (including GB2672-2017, NY659-2003 and NY/T288-2012), or WHO and EU (Table 1). This seems to indicate that the transfer of heavy metals from soil to tea in this study is "safe". Levels of eight metals were under 16 mg/kg. Some elements such as Cu and Zn, accumulated in tea easily. The accumulation of heavy metals followed the order: Zn > Cu > Ni > Pb > Cr > As > Cd > Hg. This is totally different from those in soil (Table 1). This could be related to the metabolism of plants (Kabata-Pendias and Pendias, 2001). In comparison with previous studies in China, the heavy metal contents of tea leaves were relatively lower (Chen et al., 2009; Shi et al., 2008). However, the levels of heavy metals were the similar to those observed in previous studies in the same area (Peng et al., 2018; Zhang et al., 2020). These studies showed that accumulation of heavy metals in tea plant depends on tea cultivars. Generally, the levels of heavy metals in tea leaves are under ~50 mg/kg in most cases (Karak and Bhagat, 2010). However, different cultivars, various geological condition or environment, or even different processing procedure had been found in many countries around the world to result in different levels of elements in tea (Karak and Bhagat, 2010; Malik et al., 2008). It have been known that the heavy metals in plant could come from soil, and be influenced by other factors (Kabata-Pendias and Pendias, 2001). The Pearson correlation between heavy metals in soil and tea leaves in this study was listed in Table S2. Only soil Cr, Ni were significantly correlated with tea Cr and Ni (*r* > 0.8) respectively. This proved that accumulation and transfer of heavy metals in tea from soil were influenced by other factors such as plant cultivars, geological background and etc., besides soil metals.

3.2. Factors influencing of distribution of heavy metals in soil and tea leaves

3.2.1. Soil

To understand the characteristics of heavy metals in tea garden and interaction between soil and tea, the main soil properties and geological factors, which could influence geochemical behaviors of elements were considered. These include soil pH, organic matter, soil Fe/Mn, soil type, soil bulk density, soil texture, weathering parent material, and bedrock. The Kruskal-Wallis test showed that soil arsenic distribution was significantly influenced by all of soil properties and geological factors ($p < 0.05$) (Fig. 3, Table S3) while levels of heavy metals in soil were significantly different in various soil type. This possibly indicate that various soil minerals in different soil type lead a buffer effect that controls the distribution of heavy metals in soil (Kabata-Pendias, 1995). High-levels of As, Cd, Cu, Hg, Pb and Zn occurred in red and yellow-brown soil (Fig. 3). This could be related to the geochemistry of iron and manganese hydroxides in soil (Xu et al., 2015). But except Cr and Cu, the samples with low soil Fe/Mn (<30) had significantly high concentrations of As, Cd, Hg and Pb ($p < 0.05$). This could be related to enrichment of Mn in tea (Karak and Bhagat, 2010; Karak et al., 2017). Geochemical behavior of Mn could influence the distribution of these metals in soil (Balistrieri and Murray, 1986; Xu et al., 2015). It is well-known that soil iron and manganese, and pH are commonly the driving forces for the change of redox conditions and chemical reactions involving organic matter (Bourg and Loch, 1995). In soil samples from tea garden, heavy metals showed different characteristics of distribution under acid condition (soil pH < 6.4). As shown in Fig. 3 and Table S3, only As, Cu, Ni, Pb and Zn showed significantly different ($p < 0.05$) distribution patterns at different pH. For the samples with pH < 4.5, the levels of soil As, Hg and Pb were relative higher. However, Cd, Cr, Cu, Ni and Zn accumulated in samples with pH > 4.5. This indicated that moderate acidification could enhance the mobilization and availability

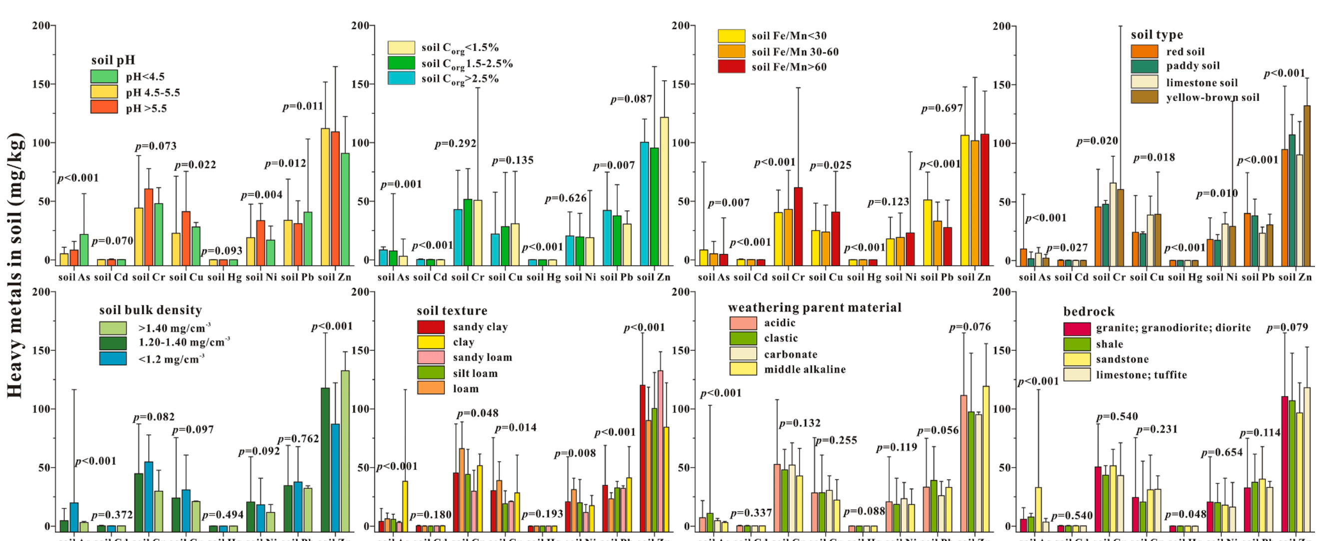

Fig. 3. Differences in the distribution of heavy metals in soil were influenced significantly ($p < 0.05$) by various soil properties (pH, organic carbon, Fe/Mn, soil type, bulk density, soil texture) and geological factors (weathering parent material, bedrock) by Kruskal-Wallis test.

of heavy metals (Yu et al., 2017).

As shown in previous studies, iron and manganese hydroxides could have different geochemical behaviors under different pH (Balistrieri and Murray, 1986; Gadde and Laitinen, 1974). Therefore, distribution of heavy metals was consistent in different pH and Fe/Mn. High soil As, Hg and Pb distributed in samples with low Fe/Mn and pH, while high Cr, Cu, Ni and Zn in samples with higher pH and Fe/Mn. As one of the participants of redox processes in soil or sediment, pH and Fe/Mn hydroxides will influence the geochemistry of organic matter (Grybos et al., 2007; Yu et al., 2017). In this study, soil with higher organic matter ($C_{org} > 2.5\%$) had high As, Cd, Hg and Pb ($p < 0.05$) (Fig. 3, Table S3). Usually, these metals are associated/complex with organic matter easily (Kabata-Pendias and Pendias, 2001). By contrast, although differences of distribution of soil Cr, Cu, Ni and Zn were not significant with change of soil organic matter, high-levels of these metals occurred in samples with relatively lower soil C_{org}.

Apart from influencing mobilization of heavy metals directly, soil organic matter also had relation with soil bulk density and soil texture (Arvidsson, 1998; Kawada et al., 2002). It can be seen that heavy metals are mainly concentrated in the samples with low bulk density. Although only As and Zn distribution were significantly different (Fig. 3). This could have resulted from negative correlation between soil organic matter and bulk density (Arvidsson, 1998). Likewise, clay or clay loam content was negatively related to soil bulk density. So heavy metals in soil are easily distributed in clay or loam part at high levels (Fig. 3) (Ma et al., 1997). By contrast, the influence of parental material and bedrock for distribution of heavy metals seemed to be minor. But heavy metals in samples with middle alkaline parent material were relatively low. In the study area, granite, granodiorite/diorite are predominant. But heavy metals in samples with sedimentary rock, such as shale and sandstone, were relatively high as in previous studies (Peng et al., 2004; Zhang et al., 2020). Generally speaking, although heavy metals in soil seemed to be decided by parent material and bedrock. The re-distribution of heavy metals in soil resulted from weathered minerals such as Fe/Mn hydroxides, clay, organic matter and other properties (Anda, 2012; Zinn et al., 2020).

As shown in Table 2, principal component analysis (PCA) results for soil identified the relation between heavy metals and specific soil properties explaining more than 70% of variances in the variables. It can be seen that PC1 could be related to soil Fe_2O_3. And Cr, Cu, Ni and a part of Zn had high positive loading on PC1, which indicated effect of Fe_2O_3 on distribution or geochemical behavior on these metals. According to the non-parameter test results in Fig. 3, the levels of soil Cr, Cu, Ni and Zn were high in the samples with soil Fe/Mn > 60. Soil Cr, Cu and Ni could be adsorbed or co-precipitated with Fe (Du Laing et al., 2009; Palumbo et al., 2001). PC2 was explained by soil Cd, Mn, pH and a part of Hg, Zn, and C_{org}. As discussed above, Cd and Hg were significantly higher in samples with soil Fe/Mn < 30 and $C_{org} > 2.5\%$ (Fig. 3 and Table S3). This result could support discussion above, which suggests that soil Cd and Hg were affected by redox reaction controlled by Fe/Mn hydroxides and organic matter. Soil Mn oxides has been proved to be the main reason for formation of humus (Shindo and Huang, 1984). The form they are bound to organic matter has been found as an important pathway for mobilization of Hg and Cd (Dong et al., 2019; Liang et al., 2013). Otherwise, different effect of soil pH on Cd and Hg could indicated that geochemical behavior of Cd could be controlled by redox reaction by Mn oxides and humus, while Hg was mainly affected by organic matter (Fig. 3). And from result in Fig. 3, distribution of soil Zn could be related to sorption or co-precipitation on Fe/Mn hydroxides under different soil pH (Gadde and Laitinen, 1974).

Except PC2, soil organic matter could be explained by PC3. (Table 2) Soil As, Pb and Hg had positive loading on PC3. It has been found that As, Pb and Hg were higher in samples with soil $C_{org} > 1.5\%$ in this study (Fig. 3). It showed the influence of organic matter on these three metals. In the studies reported before, organic matter was proved as the critical factor to control their geochemical behavior (Hernandez-Soriano and Jimenez-Lopez, 2012; Williams et al., 2011).

3.2.2. *Tea leaves*

After the transfer process, heavy metals in tea showed a totally different characteristics of accumulation (Fig. 4, Table S4). As one type of plants which prefer acid soil condition, tea plant was found to have good growth with soil pH ~4 - ~6.5 (Baruwā, 1989). In comparison with levels of heavy metals in tea leaves samples, it could be implied that the optimal pH for tea growth ranged from 4.5to 5.5 because tea As, Cd, Cu, Hg and Pb were high in the sample with soil pH 4.5–5.5. However, heavy metals in tea leaves were lower when soil pH < 4.5 (Fig. 4), although only Pb and Zn were at high levels in samples with low soil Fe/Mn. In contrast to the distribution in soil, accumulation of heavy metals in tea leaves seemed not to be affected by soil Fe and Mn (Fig. 4) due to abundant enrichment of Mn in tea through plant metabolism (Karak and Bhagat, 2010; Pohl and Prusisz, 2007). While organic matter could affect the mobility and transfer process of heavy metals from soil to tea, low levels of heavy metals are distributed in tea leaves with soil C_{org} of 1.5–2.5%. Distribution of high tea As, Cu and Ni in samples with $C_{org} <$ 1.5% were different from Cd, Pb and Zn. This could indicate that there are differences in the factors influencing the transfer process of these two groups of metals. Under appropriate soil pH, mobility and transfer of Cd, Pb and Zn could be related to both soil organic matter and Fe/Mn hydroxides (Grybos et al., 2007; Zhang et al., 2014). Accumulation of As, Cu and Ni in tea could be influenced by Fe hydroxides more (Grybos et al., 2007). The differences between distribution of heavy metals in tea leaves which changed under various soil pH, C_{org} and Fe/Mn ratio also reflected in the sample with different soil types. The tea growing in paddy soil and yellow-brown soil had relatively higher heavy metals (Fig. 4). This could imply that transfer and accumulation of heavy metals

Table 2
Principal component analysis (PCA) with varimax rotation to characterize the distribution of heavy metals in tea and soil samples by eigenvalue and loadings of heavy metals on different PCs.

tea	PC1	PC2	PC3	**soil**	PC1	PC2	PC3
eigenvalue	3.220	2.236	1.738	eigenvalue	3.640	2.476	2.438
variance%	40.245	27.952	21.720	variance%	30.331	20.637	20.316
As	0.755	0.289	0.438	As	0.036	−0.112	0.865
Cd	0.916	0.099	0.158	Cd	−0.268	0.811	0.273
Cr	0.233	0.943	0.040	Cr	0.872	0.061	−0.124
Cu	0.376	0.470	0.689	Cu	0.765	−0.010	0.307
Hg	0.798	0.268	0.438	Hg	−0.601	0.388	0.411
Ni	0.066	0.972	0.089	Ni	0.863	0.191	−0.168
Pb	0.908	0.094	0.342	Pb	−0.144	0.035	0.881
Zn	0.386	−0.091	0.853	Zn	0.352	0.567	−0.362
				Fe_2O_3	0.863	0.040	−0.242
				Mn	0.071	0.864	0.053
				C_{org}	−0.404	0.465	0.519
				pH	0.238	0.573	−0.267

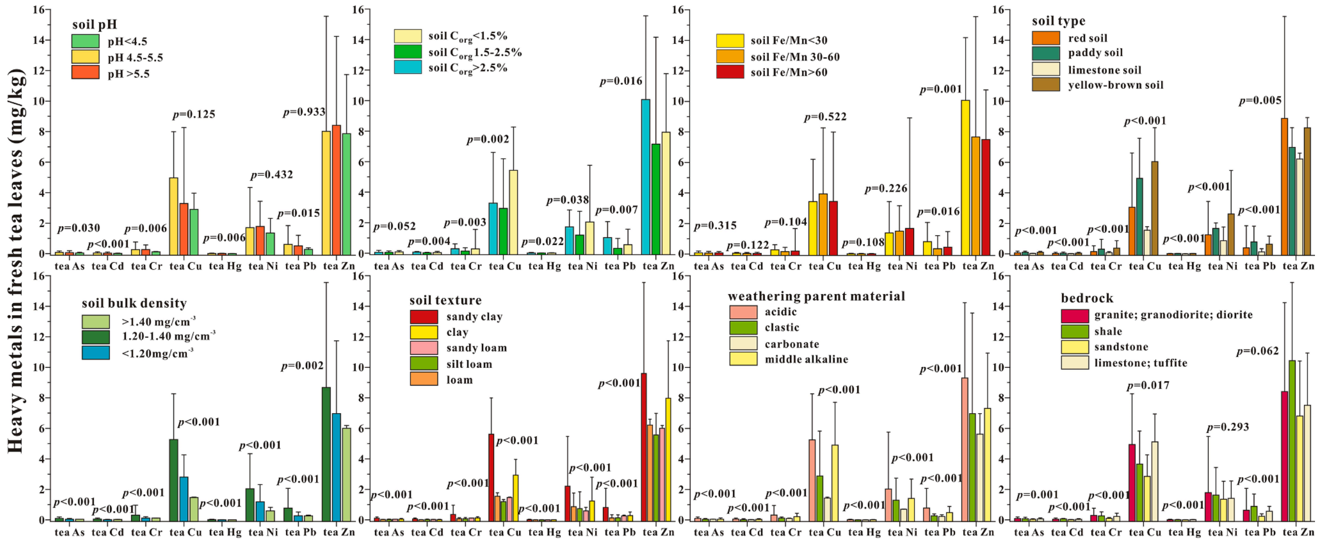

Fig. 4. Differences in the distribution of heavy metals in tea leaves were influenced significantly ($p < 0.05$) by various soil properties (pH, organic carbon, Fe/Mn, soil type, bulk density, soil texture) and geological factors (weathering parent material, bedrock) by Kruskal-Wallis test.

from soil to tea was influenced by adsorption and redox reaction caused by organic matter and Fe/Mn hydroxides (Grybos et al., 2007). The high Zn level in tea growing in red soil indicate that Zn transfer was mainly controlled by Fe/Mn hydroxides.

Accumulation of heavy metals in tea leaves was significantly high under condition of medium soil bulk density (Fig. 4). This implied that transfer and accumulation of heavy metals in tea were closely related to tea plant growth. Therefore, moderate growth condition seemed to be helpful for accumulation of heavy metals in tea leaves. This could also be the reason why levels of heavy metals in the tea samples growing in soil with sandy clay are relatively high ($p < 0.05$) (Fig. 4). Different from distribution in soil, the main source of heavy metals in tea were geological background (Zhang et al., 2020). So the heavy metals in samples with acidic parent material and granite/granodiorite/diorite were high due to weathering. And shale could be thought as another source for As, Cd, Pb and Zn, as well as limestone/tuffite for Cu.

For tea leaves samples, PCA results was slightly different from that of soil samples (Table 2). All heavy metals had positive loading on PC1. And PC1 mainly explained the variation of As, Cd, Hg and Pb. From the discussion above about distribution characteristics of heavy metals in tea leaves, it could be seen that tea As, Cd, Hg and Pb in samples with soil pH 4.5–5.5 were significantly high (Fig. 4). While these elements had same distribution in samples with different soil C_{org} and low Fe/Mn ratio. This implied that PC1 could be related to soil redox process except tea plant metabolism, which influenced the availability and accumulation of As, Cd, Hg and Pb from soil to tea leaves.

Tea Cr, Cu, Ni and Zn were reflected by PC2 and PC3 (Table 2). These four metals were found to be affected by pH by non-parameter test (Fig. 4). But unlike the metals which were explained by PC1, high-level Cr, Ni and Zn in tea leaves were distributed in samples with pH > 5.5. Meanwhile, tea Cr and Ni were relatively high in samples with middle-alkaline parent material. It can be concluded that PC2 is related to the weathering of parent material for Cr and Ni as typical siderophile elements. It was why tea Cr and Ni were slightly high in samples with soil Fe/Mn > 60 and yellow-brown soil. During weathering, Fe hydroxides reduction could influence accumulation of Cr and Ni from soil to tea (Grybos et al., 2007). And during this process, coprecipitation and release with Fe/Mn hydroxides could control mobility of soil Ni. Because more than 20% of total soil Ni was Fe-Mn oxides bound fraction in the samples with high level of free Fe (Golui et al., 2020). PC3 showed characteristics of tea Zn and Cu mainly (Table 2). These two metals were at higher levels in tea leaves than other elements (Table 1). Under different soil pH, distribution of tea Cu and Zn were not significantly different (Fig. 4). From the results in Fig. 4, accumulation characteristics of tea Zn and Cu were not clear. Because Zn or Cu had similar distribution to other elements, this could be explained by the metabolism of tea plant (Chen et al., 2009; Kabata-Pendias and Pendias, 2001). While plant availability of Cu and Zn could increase with decreasing soil pH (Planquart et al., 1999). Therefore, PC3 might represent uptake effect of tea plant under acidic soil condition with various multiple properties.

3.3. Influence factors analysis for transfer of heavy metals from soil to tea leaves by CART

Different results for distribution of heavy metals in soil and tea by non-parameter test and PCA indicated that the transfer process affected the accumulation characteristics of heavy metals in tea. To investigate the factors influencing the transfer process of heavy metals in tea garden, plantation, soil properties and geological background as shown in Table S1 were integrated into CART to understand influencing factors for TF. The results of CART showed that clones of tea type were the most important variable-splitting factors for the transfer factors of As, Hg and Zn (Fig. 5). It can be seen that samples of type 4 had higher TF values for As and Hg, and lower value for Zn. This could indicate that tea sample of type 4 accumulates As and Hg easily. As shown in Figure S1, all metals in tea and soil samples were significantly different for clone of tea types. Heavy metals tended to enrich into tea samples of type 1 and 4 easily. Otherwise, besides high levels of heavy metals in soil with type 1 or 4 tea, As, Cu, Hg and Pb also accumulated in soil samples used for growing of type 3 tea. Generally, it could be calculated that high TF values of heavy metals occurred in tea samples of type 1 and/or 4. And TF values in tea samples of type 4 were the highest for As, Cd, Hg and Pb, while those in type 1 samples were highest for Cr, Cu and Zn. TF-Ni were high in both type 3 and 4 samples. This result was similar to the PCA of tea samples, which implied that the transfer of elements were in accordance with their distribution in tea plant.

While the same nodes in CART to As and Hg were soil C_{org}. This indicated the effect of soil organic matter on transfer process. Mobility of As and Hg has been found to combine with methylated process of organic matter closely (Kabata-Pendias and Pendias, 2001). And in accordance with distribution of As and Hg in tea and soil, high transfer factor values occurred in the samples with low C_{org}, which could be controlled by redox reaction of organic matter (Fig. 5) (Grybos et al., 2007). For As, TF values in the samples with acidic parent material were

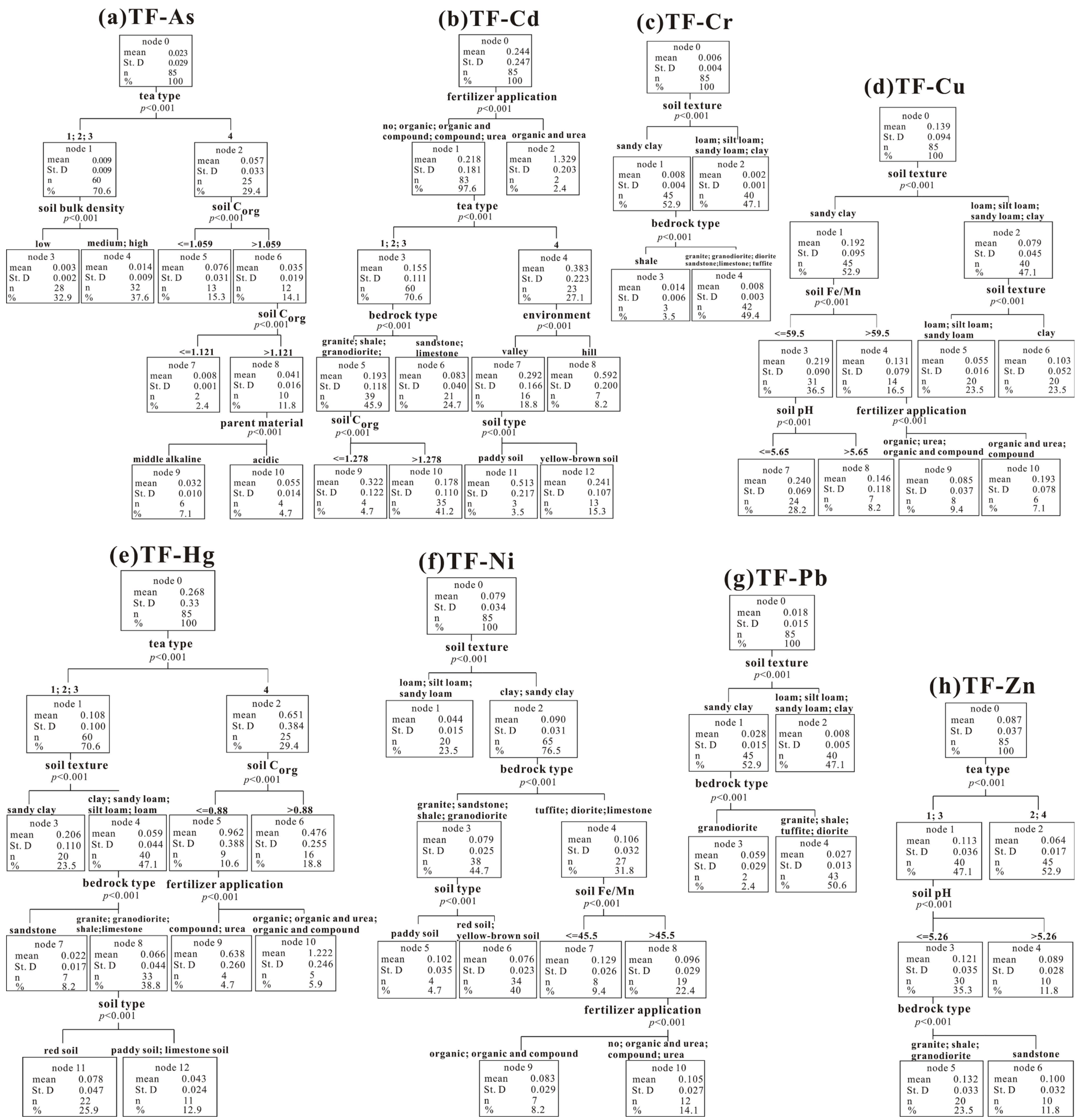

Fig. 5. Decision tree with CART method for the transfer factors (TF) of heavy metals from soil to tea.

higher than those of middle alkaline parent material. This implied soil As could come from acidic parent material mainly and transfer to tea easily (Figs. 3 and 4). For Hg, fertilizer application was found to help Hg transfer under low soil C_{org} (Fig. 5) (Karak et al., 2017). But soil pH was the main splitting factor for the transfer of Zn after tea type, in accordance with the PCA analysis result (Table 2). As found in previous research, Zn accumulated in tea plant easily under low pH (Fung and Wong, 2002).

In CART, transfer factors of Cr, Ni and Pb had the same splitting factors as soil texture and bedrock at similar nodes (Fig. 5). As discussed above, with sandy clay, Cr, Ni and Pb were significantly enriched in tea leaves (Fig. 4). It is noteworthy that Richards et al reported that the short- and long-term mobility of heavy metals in coarse-textured soil with high plant yield was higher than fine-textured soil (Richards et al., 2000). This could be the reason why sandy clay presents a moderate soil texture for tea plant growth (Planquart et al., 1999; Richards et al., 2000). Although high transfer factors for Cr, Ni and Pb occurred in the same soil texture condition. They were different under various bedrock type. According to some studies, weathering of specific basic/ultrabasic rock could be the natural source for soil Cr and Ni (Anda, 2012; Kelepertzis et al., 2013; Zinn et al., 2020). Low levels of Cr and Ni in soil on the top of granite was also found in Africa (Zhai et al., 2003). But in contrast, Pb seemed to be higher in the soil developed on the granite in these studies. For different types of rock in the upper continental crust, Pb levels are relatively lower in basic rocks (Hu and Gao, 2008). This could be the reason why transfer factor was slightly higher in samples with granodiorite, but lower value for Cr and Ni (Fig. 5). According to results from sequential extraction, except the residual part, Fe/Mn hydroxides bound fraction was thought as the main form of soil Ni (Golui et al., 2020; Zhai et al., 2003). A high proportion of this fraction occurred in the sample with high free Fe indicating that mobility of Ni could be controlled by Fe/Mn hydroxides (Golui et al., 2020). As shown in Fig. 5, the transfer factor for Ni was higher in the samples with soil Fe/Mn < 45.5. This could be result in the reducing effect of Fe hydroxides, accompanied with sorption by Fe/Mn hydroxides (Golui et al., 2020; Grybos et al., 2007).

Similar to the Cr, Ni and Pb, TF-Cu was also split firstly by soil texture (Fig. 5). High TF value in samples with sandy clay resulted in enrichment of Cu in tea leaves as shown in Fig. 4. According to the PCA results for metals in tea leaves, accumulation characteristics of Cu in tea seemed to be complex, although high Cu levels were distributed in soil with Fe/Mn > 60 (Table 2). This implied that the transfer process of Cu from soil to tea was related to the state change of redox state which is commonly caused by pH, Fe/Mn hydroxides, organic matter and etc. So following soil texture, soil Fe/Mn is the second factor influencing TF-Cu (Fig. 5). Same as in previous studies, mobility and bioavailability of Cu seemed to be complex and unclear (Golui et al., 2020; Grybos et al., 2007). As discussed above and by the results in Figs. 3 and 5, soil Cu could be held by Fe hydroxides (Du Laing et al., 2009). So high TF-Cu occurred in the samples with soil Fe/Mn < 59.5 (Fig. 5). And at low soil pH, it is easy for soil Cu to move from soil to plant (Planquart et al., 1999) while redox reaction caused by Mn hydroxides and organic matter could help Cu enter tea plant (Grybos et al., 2007).

PCA results showed that distribution of Cd and some other metals in soil and tea seemed to be related to other factors. However, transfer process of Cd from soil to tea was different from other heavy metals (Fig. 5). The most important influencing factor was fertilizer application. Fertilizer application has been found to enrich Cd in rice plant easily (Huang et al., 2018; Song et al., 2018). Long-term utility of fertilizers could increase the health risk to human through crop consumption (Hosseini Koupaie and Eskicioglu, 2015). It can be seen that only 2 samples were split into node 2 (Fig. 5). Most samples were put into the same node, which implied that fertilizer application helped transfer of Cd from soil to tea. Fertilizer has been found as a main source for heavy metals in tea (Karak et al., 2017). However, organic/inorganic fertilizer or soil amendments could immobilize heavy metals through pH increase with the help of hydroxyl and carboxyl groups (Hamid et al., 2018; Hamid et al., 2019). In this study area, various fertilizer application managements were used (Table S1). Besides Cd, fertilizer application had significant effect on the extraction of heavy metals by tea plant. Thus, relatively high-levels of heavy metal accumulation in tea samples occurred when no fertilizer, urea and/or organic and urea was applied (Figure S1). As in previous studies, urea has been found to enhance uptake of heavy metals by different plants or crops (Ji et al., 2020; Shtangeeva et al., 2004). Likewise calculated TF values were highest in the samples with no fertilizer, urea and/or organic and urea application. Therefore, it can be inferred that organic and/or compound fertilizer could reduce transfer of heavy metals from soil to tea under acidic conditions. Meanwhile, distribution of As, Cd, Cu, Hg, Pb and Zn in soil were significantly different (Figure S1). But these distributions appeared to have no relationship to fertilizer application. The possibility cannot, however, be excluded that fertilizer application made soil Cd and other heavy metals much higher, although below standard limits, than the background value (Table 1).

Clones of tea type were the second influencing factor for transfer of Cd. Similar to As and Hg, type 4 tea samples enriched Cd easily, which implies that type 4 clones are susceptible to accumulation of heavy metals. After fertilizer and the clone of tea type, plantation environment and bedrock also affected transfer of Cd. Good drainage is good for tea plant growth (Baruwā, 1989; Mondal, 2009). So the TF-Cd in samples growing on the hills were higher than those in the valley (Fig. 5). Meanwhile, in accordance with results of non-parameter test in Fig. 4, tea samples in area with bedrock of granite/granodiorite and shale had high TF values for Cd.

CART method has previously been used to interpret the characteristics of spatial change and source identification of heavy metals in soil through correlation between heavy metals in soil and other environmental variables (Wu et al., 2020; Zhong et al., 2014). An advantage of CART method is that it could interpret the correlation between specific numeric/nonnumeric variables and TF values of heavy metals from soil to tea well. Based on this method, the main influencing factors were identified for the transfer of heavy metals from soil to tea. Although many possible plantation factors, soil properties and geological background that could be relate to the transfer and accumulation of heavy metals in tea plants were taken into account, some effects caused by these factors could be missed or marred by other factors. Except for direct investigation through splitting variables, the importance of variables in CART could reflect the influence of specific variables on all split for each TF (Table S5). Generally, the clones of tea type showed the biggest effect on transfer and mobility of heavy metals in tea garden. But it is geological bedrock that decides the levels and transfer of heavy metals as well as soil properties that lead to the transfer of different heavy metals. Besides, soil texture and fertilizer application were also influence the transfer process of heavy metals in soil-tea system. From the CART analysis, it can be concluded that the clones of tea type should be selected for tea plantation management while carefully considering geological backgrounds with various bedrock types. On the other hand, fertilizer application is the main anthropogenic activity that affect the transfer of heavy metals.

3.4. Potential human health risk assessment through tea consumption

Through human health risk assessment, the potential harm to human through tea drinking can be assessed quantitatively. According to a protocol from US EPA, the average daily intake (ADI) values of some heavy metals through tea drinking are shown in Table 3. The daily intake of Cu, Ni and Zn were the highest (usually of the order of 10^{-3} mg/kg (body weight) $\cdot$ day), followed by Cr and Pb ($\sim 10^{-4}$ mg/kg (body weight) $\cdot$ day). The ADI values are at the same levels as those in previous studies (Peng et al., 2018; Zhang et al., 2020). For drinking water, TDI (500 μg/kg for Cu, 2 μg/kg for Hg and 12 μg/kg for Ni) or PTMI (25 μg/kg for Cd and 4 μg/kg(weekly) for Hg) proposed by FAO/WHO (JECFA, 2019). In this study, calculated ADI values were further lower than TDI and PTMI limits. According to the WHO, drinking water is thought to be safe, when As < 0.01 mg/L, Cd < 0.003 mg/L, Cr < 0.05 mg/L, Cu < 2 mg/L, Hg < 0.006 mg/L, Ni < 0.07 mg/L and Pb < 0.01 mg/L (World Health Organization, 2017). If a 60-kg adult drinks 2 L water every day (FAOSTAT, 2020; World Health Organization, 2017), then the intake of As < 0.02 mg, Cd < 0.006 mg, Cr < 0.1 mg, Cu < 4 mg, Hg < 0.012 mg, Ni < 0.14 mg and Pb < 0.02 mg one day by one adult can be tolerable. As the most popular beverage in Asia, especially China, the consumption of green tea is only about 11.4 g per day (Peng et al., 2018). The calculated average daily intake amounts of heavy metals through tea consumption in this study for an adult are: 0.0009 mg for As, 0.00052 mg for Cd, 0.0041 mg for Cr, 0.046 mg for Cu, 0.00014 mg for Hg, 0.025 mg for Ni, 0.0073 mg for Pb and 0.099 mg for Zn. So daily consumption of tea product from the study area is safe. However, intake of heavy metals in tea infusion could potentially lead to accumulative human health risk. (de Oliveira et al., 2018; Zhang et al., 2020).

As shown in Table 3, HQ values followed the order: Pb ≫ As > Ni > Cu > Hg > Cd > Zn ≫ Cr. Only mean value of HQ for Pb (1.939) exceeded 1, which accounted for>85% of total HQ (THQ) (Figure S2 (A)). This indicated that non-carcinogenic health risk to human appeared to be mainly caused by Pb in tea through oral ingestion pathway. The reference dose (RfD) of Pb is not determined and given officially, so the HQ values calculated using Pb in tea were relatively lower in other studies, although levels of Pb in tea were higher than in this study (Peng et al., 2018; Zhang et al., 2020). The RfD (0.00014 mg/kg·day) for Pb proposed by Oak Ridge National Laboratory, US seems to be the most stringent, which was used in this study (Qu et al., 2012).

Table 3
The average daily intake (ADI) (mg/kg (body weight)·day) of heavy metals and non-carcinogenic risk (HQ) and carcinogenic risk (Risk) for people caused by tea drinking.

	ADI			HQ			Risk		
	min	max	mean	min	max	mean	min	max	mean
As	1.47×10^{-5}	6.07×10^{-5}	3.50×10^{-5}	0.049	0.202	0.117	2.20×10^{-5}	9.11×10^{-5}	5.25×10^{-5}
Cd	6.04×10^{-6}	6.40×10^{-5}	2.07×10^{-5}	0.006	0.064	0.021	9.06×10^{-5}	9.59×10^{-4}	3.10×10^{-4}
Cr	3.54×10^{-5}	1.06×10^{-3}	1.57×10^{-4}	0.000	0.001	0.000	1.77×10^{-5}	5.30×10^{-4}	7.87×10^{-5}
Cu	8.20×10^{-4}	3.87×10^{-3}	1.87×10^{-3}	0.020	0.097	0.047			
Hg	8.22×10^{-7}	1.17×10^{-5}	5.08×10^{-6}	0.005	0.073	0.032			
Ni	2.57×10^{-4}	5.46×10^{-3}	1.08×10^{-3}	0.013	0.273	0.054			
Pb	6.57×10^{-5}	8.22×10^{-4}	2.71×10^{-4}	0.469	5.872	1.939	5.58×10^{-7}	6.99×10^{-6}	2.31×10^{-6}
Zn	2.48×10^{-3}	8.48×10^{-3}	4.38×10^{-3}	0.008	0.028	0.015			
totalΣ				0.648	6.265	2.224	1.68×10^{-4}	1.23×10^{-3}	4.44×10^{-4}

According to previous reports, infusion rate of heavy metals varied with clones of tea and changed in different cases (de Oliveira et al., 2018; Karak and Bhagat, 2010; Schmite et al., 2019). For example, the infusion rate for As changed between 11–45%, 14–52.8% for Cd, 4–28.7% for Cr, and 10.1–75.6% for Pb in various tea samples. So there seems to be no fixed infusion rates for specific teas. Monitoring for total levels of heavy metals in tea leaves is therefore necessary and possibly more effective.

Linear correlation between TF values from soil to rice and heavy metals in rice has been found (Mao et al., 2019). For tea plant, an exponential correlation between TF from soil to tea and heavy metals in tea is displayed in Fig. 6. For HQ value with 1, the tea Pb level was calculated as 0.758 mg/kg and TF = 0.023 in this study. Pb level in about over 50% of samples were below 0.758 mg/kg, although the average HQ of Pb exceeded 1. To avoid non-carcinogenic health risk in this study area, effective and feasible investigation for the main factors influencing Pb transfer from soil to tea should be carried out, especially soil texture. As discussed above, besides Pb, samples in areas with bedrock type of granite/granodiorite and shale could have high heavy metals in tea leaves and TF values. Thus, more attention should be paid to tea gardens in areas with granite/granodiorite and shale.

For carcinogenic risk, As, Cd, Cr and Pb in tea samples were taken into account (Table 3). Carcinogenic risk of tea Cd and Cr were higher than those of As and Pb. The risk level of Cd reached unacceptable level with a risk value of 3.1×10^{-4}, which accounted for 69.93% of total carcinogenic risk ($Risk_{total}$) (Figure S2(B)). This means that 31 per 100,000 adults could be exposed to cancer risk by Cd through tea drinking. The risk levels of As and Cr were acceptable/tolerable with mean risk values of 5.25×10^{-4} and 7.87×10^{-4}, respectively. Unlike non-carcinogenic risk, Pb in tea was at an acceptable level for carcinogenic risk. This indicated that Pb in tea in this study area seemed to only cause accumulative non-carcinogenic adverse effect on human. As shown in Fig. 6, the risk value of As in all tea samples varied from 10^{-6} to 10^{-4}, which means cancer risk caused by As was acceptable. For Cd, tea samples with tea Cd > 0.036 mg/kg and TF > 0.176 had potential carcinogenic risk (Risk > 10^{-4}). To reduce or avoid carcinogenic risk by Cd in tea leaves, specific fertilizer should be selected as discussed in CART, such as organic and/or compound fertilizer. Tea products from tea gardens in the hill with granite/granodiorite and shale must be given more monitoring, and other remediation operation such as pH adjustment. In the case of Cr, cancer risk was unacceptable when Cr is tea was above 1.082 mg/kg with TF > 0.023 (Fig. 6). In the CART analysis, the transfer of Cr and Pb was mainly affected by soil texture and bedrock type. Thus, changing soil texture through soil amendments and monitoring in areas with granite/granodiorite and shale could help to reduce carcinogenic and non-carcinogenic risk to human health caused by the transfer of Cr and Pb from soil to tea.

4. Conclusion

An exponential decrease with the ratios of metals in soil to PM and heavy metals in PM Indicated weathering pedogenic process is the main source of heavy metals in tea gardens. While Cd, Hg, Pb and Zn in over 75% of soil samples were above background levels. However the tea samples were safe with heavy metals levels below limits of China, WHO and EU standards. Distribution of heavy metals in soil and tea were influenced by soil properties significantly. Result of non-parameter test and PCA implied that distribution and transfer of As, Cd, Hg and Pb in soil and tea could be affected by soil organic matter and redox process.

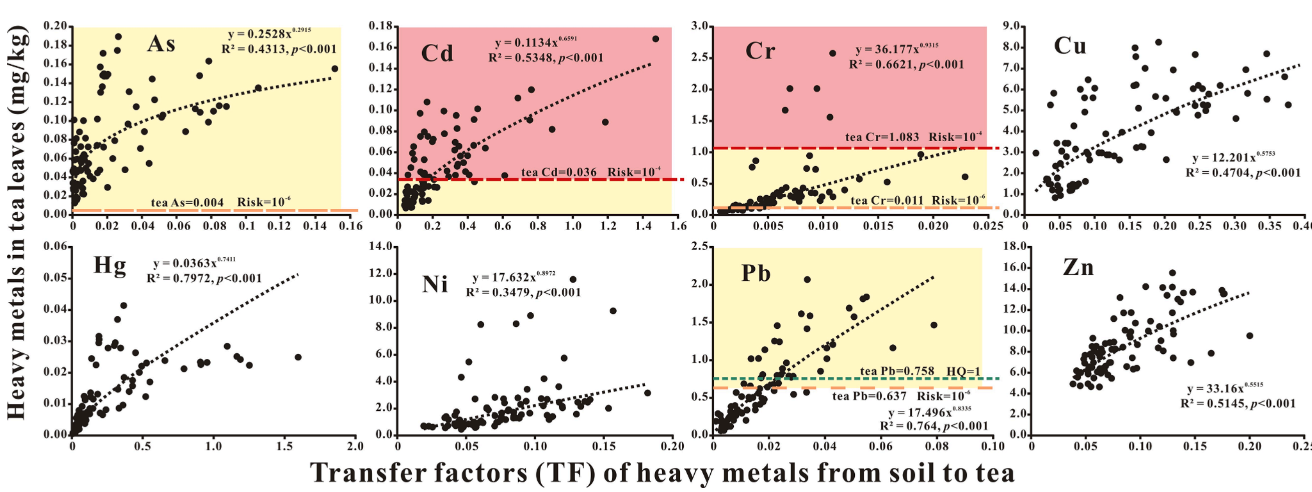

Fig. 6. Increasing heavy metal levels in tea leaves with increasing transfer factor (TF) of heavy metals from soil to tea. Only HQ values calculated for Pb (>0.758 mg/kg) were over 1 and the cancer risk (Risk) for As, Cd, Cr and Pb were acceptable in the "yellow area" and unacceptable in the "red area". (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Geochemical behaviours of Cr, Cu, Ni and Zn in tea garden were mainly controlled by pH and iron oxides.

CART results showed that clone of tea type could be the first factor to decide the transfer of heavy metals from soil to tea. The soil conditions that are good for tea growth, such as soil texture and organic matter, can enhance the transfer of heavy metals. Bedrock type was found to be the biggest influencing factor from geological background. Granite/granodiorite and shale were geological sources of heavy metals in soil and tea in this study. Fertilizer application was the biggest anthropogenic source and factor to influence the transfer of metals. Organic/compound fertilizer displayed an immobilizing effect on transfer of heavy metals in tea garden.

According to health risk assessment, people could be exposed to non-carcinogenic health risk caused by the presence of Pb in tea, which accounted for over 85% of total non-carcinogenic risk. From the CART analysis, more attention should be paid to monitoring non-carcinogenic risk for tea products from areas with sandy clay and geological background with granite/granodiorite. The concentration of Cd accounted for about 70% of total carcinogenic risk, reaching an unacceptable level while the cancer risk level by the presence of As, Cr and Pb in tea were mostly acceptable.

Generally, to reduce cancer risk through tea drinking, more attention and monitoring needs to be given to the soil texture especially sandy clay and geological background particularly granite/granodiorite and shale while. Organic and/or compound fertilizer could be selected to immobilize the transfer and accumulation of Cd and other metals in tea leaves.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catena.2021.105419.

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