Article

Accumulation and Health Risk Assessment of Heavy Metal(loid)s in Soil-Crop Systems from Central Guizhou, Southwest China

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Abstract: Heavy metal(loid)s (HMs) contamination in agricultural soil and crops is related to the quality and safety of agricultural products and public health and has attracted worldwide attention. This study systematically investigated the bioaccumulation of HMs including Cd, Pb, Cr, Hg, As and Se in soil and associated crops (Tea, Plum and Corn) in Guizhou Province, China, and assessed the health risks of the edible part of the crops using the bioconcentration factor (BCF), geoaccumulation index (Igeo), and target hazard quotient (THQ). The results indicate that the mean concentrations of Pb (39.54 ± 16.56 mg/kg), Cr (122.50 ± 33.36 mg/kg), Hg (0.26 ± 0.33 mg/kg), As (25.40 ± 21.34 mg/kg), and Se (0.90 ± 0.46 mg/kg) in cultivated soil exceed the background values of Guizhou Province by 1.12, 1.28, 2.36, 1.27, and 2.4 times, respectively. However, the average concentration of Cd is 0.49 ± 0.49 mg/kg, which is lower than the corresponding background value. The average Igeo values of Pb, Cd, Cr, and As in the soil samples were lower than 1, indicating a relatively low degree of enrichment, whereas the enrichment of Hg was relatively obvious, as approximately 32.9% of the samples were at moderate and above enrichment levels. The contents of HMs in samples of corn, plum, and tea were lower than the corresponding pollutant limit. The BCF values of tea in the soil-crop system were higher than those of corn and plum. Correlation analysis showed that the soil pH and concentrations of K2O, Fe2O3, and Al2O3 were negatively correlated with the BCF of Pb, Cd, Cr, and Hg in the soil-crop system, indicating that they were affected by macro-oxidation in the soil, whereas Cd and As were basically not affected. The human health risk assessment of THQ values demonstrated that the health risks to local residents from eating corn and drinking tea were low.

Keywords: heavy metal(loid)s; accumulation; soil-crop system; health risk assessment

1. Introduction

As an important part of the terrestrial ecosystem, soil is the natural resource for agricultural production and human survival, as well as the guarantee of food and ecological environment security [1–3]. Soil quality is the foundation of agricultural sustainable development. In recent decades, the intensive industrial and agricultural activities have triggered heavy metal(loid) (HMs) contamination in agricultural soils [2,4,5]. The United States Environmental Protection Agency (USEPA) has classified cadmium (Cd), chromium (Cr), arsenic (As), mercury (Hg), lead (Pb), copper (Cu), zinc (Zn), and nickel (Ni) as priority pollutants [6], owing to their high toxicity, persistent nature, and bioaccumulative and irreversible characteristics [5,7]. HMs in the soil may affect human health through three exposure pathways: direct ingestion, dermal contact, and inhalation [4,8,9]. The human
health impact of HM exposure has been revealed by numerous studies. HM exposure can affect the human central nervous system and damage blood components, the lungs, liver, kidneys, and other vital organs. Once repeatedly exposed in the human body for a long time, HMs can even interfere with the endocrine and reproductive systems, and eventually lead to cancer [10]. For example, chronic exposure to Cd damages human kidneys, liver, and bone tissues [11]. The accumulation of Hg in adipose tissues after long-term exposure and can damage the brain, vision, and human central nervous system [11,12]. According to the results of China's first nationwide soil pollution survey, 19.4% of cultivated land soils had the heavy metals exceeding the standard, of which Cd, As, and Hg were the major polluting elements [13]. An enhanced accumulation of HMs in agricultural soil will affect the quality and safety of agricultural products, and even pose a serious threat to human health; thus, they have drawn great public concern [1,2,4,9,14].

Both geological processes and anthropogenic activities are considered important sources of HMs accumulation in agricultural soil [7,15,16]. Geological parent rock weathering and soil-forming processes are considered important natural sources of HMs in the soil [17,18]. Anthropogenic activities, such as industrial emissions, fertilizers and pesticides application, sewage irrigation, atmospheric deposition, and transportation [5,16,19] currently have increased amounts of HMs in soil significantly. Many previous studies have shown that excessive HMs in agricultural soil not only adversely affect the growth of crops but also accumulate in crops through root absorption, and transport to different parts of crops organs [20], especially to the parts that are consumed by or edible for humans, and ultimately enter the human body through the soil–crop–human body food chain and pose a potential threat to human health [5,21,22]. The migration of HMs in the soil–crop system is a complicated process, besides being affected by the geochemical properties of the elements [18], it is also affected by soil pH, organic matter, HMs speciation, redox conditions, cation exchange capacity, hydrological conditions, meteorological conditions, crop varieties, and interaction between elements [9,23]. Additionally, the absorption and enrichment of HMs by crops will be affected by specific oxides in the soil [9,23]. The high content of essential elements in the soil (such as Ca, Fe, and Mg) can greatly lower the rate of HMs absorption by the crop [24]. Hence, the identification of the factors influencing the migration process of HMs in the soil–crop system and their health risks is critical to the prevention and control of HMs contamination.

Guizhou Province, located in Southwest China, is a typical karst area, with 91.7% of cultivated land distributed in karst mountainous areas [25]. Due to the special geological background, HMs in the soil in this region have highly natural background attributes, and their sources and controlled factors are extremely complex [9,26,27]. Baihua Reservoir (BH), as the first-level water source, lies in Guiyang city, the capital of Guizhou Province, and the BH Basin is an important crop-planting areas. The ecological environment of the basin has attracted wide attention from the government and the public since HMs in soils can enter the water system through rainwater leaching and surface runoff, posing a threat to regional water environment quality and drinking water safety [12,28]. Due to the special geological background in this area, the natural background values of HMs in soil is relatively high [8,26,27]. In particular, the concentration of As in regional soils is significantly higher than the corresponding soil As background value in Guizhou Province [26]. Moreover, numerous industrial and mining enterprises are located near the BH Basin, including the Guizhou Organic Chemical Plant (GOCP), Guizhou Aluminium Plant (GAP), and several small-scale coal mines [28]. Industrial activities are also important sources of the accumulation of HMs in the soil. The majority of previous studies have focused on HM contamination in sediments, but investigations into HMs
in agricultural soil–crop systems are rarely undertaken. Therefore, it is of great significance to clarify the concentrations and health risks of HMs in the surrounding soil–crop system of the BH Basin for environmental quality control and the health of local residents.

The main objectives of the present study are (1) to clarify the accumulation of HMs in agricultural soils and crops in the BH Basin; (2) to explore the effects of the physical and chemical properties of the soil and the migration of HMs in the soil-crop system; and (3) to evaluate the health risks of the edible parts of crops to local residents. The results of this study provide basic scientific data on HMs in soil–crop systems in typical karst areas.

2. Materials and Methods

2.1. Study Area

The Baihua Reservoir Basin (106°27′–106°34′ N, 26°35′–26°42′ E) is located in the central part of Guizhou Province, a typical karst region in China (Figure 1). The study area includes important agricultural planting areas in Central Guizhou, and the main crops grown in this field are corn, rice, fruits, tea, and vegetables. The typical soil type is mainly yellow soil and paddy soil. The parent materials of the soil in the study area are mainly Triassic dolomite and Permian limestone, as well as a small amount of sand-bearing shale.

Field sampling activities were conducted in June and August 2018. A total of 15 tea samples, 15 plum samples, 55 corn seed samples, and 85 corresponding root soil samples were collected. Corn and plum samples were picked during the peak harvest period, and the edible parts were collected and mixed to form a sample. The tea samples were randomly selected from multiple plants in the same plot, and the leaves of the upper, middle, and lower parts of each plant were collected and mixed to form a sample. For each root soil sample, approximately 1 kg of soil made up four subsamples (0–20 cm soil depth). The soil and crop samples were packaged in clean plastic bags and then transported to the laboratory for processing. All crop and soil samples were air dried, ground with an agate mortar to pass through 10-mesh and 100-mesh sieves, respectively, and then stored in sealed bags for analysis.

Six metal elements (Pb, Cd, Hg, As, Cr, and Se) in the soil that have an impact on crop safety and physical and chemical indicators of soil (pH, organic matter, Fe, Al, Ca, Si,
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Na and Mg) that may affect their migration in the soil-crop system were selected as the object of analysis. The soil pH was measured on a mixing soil with deionized water at 1:2.5 (w/v) after stirring for 2 min and letting it stand for 30 min; the pH was determined using a Leici pH meter (PHS-3C, Shanghai, China). The determination of soil organic matter (OM) adopts the standard NY/T 1121.6-2006 issued by Ministry of Agriculture of China. In preparation for analysis, approximately 0.1 g of each soil sample was digested using 3 mL concentrated nitric acid (HNO$_3$) and 1 mL concentrated hydrofluoric acid (HF) in PTFE sealed digestion tanks for 12 h at $180 \pm 5^\circ$C. The digestion of crop samples was carried out by microwave digestion; approximately 0.5 g of dried samples were weighed in the tube and digested in a mixture containing 3 mL HNO$_3$ and 1 mL HClO$_4$ at $180 \pm 5^\circ$C for 6 h. After digestion, the concentrations of Pb, Cd, and Cr in the soil and edible parts of the crops were analyzed using inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher X2, Waltham, MA, USA), and the concentrations of As, Hg, and Se were measured using atomic fluorescence spectrometry (AFS-3100, Beijing Haiguang Instrument Corporation, Beijing, China). In addition, the contents of major elements (Fe$_2$O$_3$, Al$_2$O$_3$, CaO, SiO$_2$, Na$_2$O and MgO) in the soil were determined using an X-ray fluorescence spectrometer (XRF-ZSX Primus IV).

2.3. Quality Assurance and Quality Control (QA/QC)

QA/QC for data analysis, blanks, duplicates, and reference materials (GSS-2-14) were conducted. The results for blanks were all lower than the detection limit of the instrument. The recoveries of the reference materials were between 90% and 110%. The relative deviations of duplicates were less than 8%.

2.4. Bioconcentration Factor (BCF)

To characterize the adsorption and accumulation effect of HMs in crops from the soil [17], the bioconcentration factor (BCF) of crops was calculated as shown below:

$$ BCF = \frac{C_{crops}}{C_{soil}} $$

where $C_{crops}$ is the concentrations of individual elements in the crops (mg/kg), and $C_{soil}$ represents the corresponding value in the soil (mg/kg). The categories of BCF are summarized in Table 1.

Table 1. Classification criteria for the bioconcentration factor (BCF).

<table>
<thead>
<tr>
<th>BCF Value</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>$BCF &lt; 0.01$</td>
<td>Very weak intake</td>
</tr>
<tr>
<td>$0.01 &lt; BCF &lt; 0.1$</td>
<td>Weak intake</td>
</tr>
<tr>
<td>$0.1 &lt; BCF &lt; 1$</td>
<td>Moderate intake</td>
</tr>
<tr>
<td>$BCF &gt; 1$</td>
<td>Strongly intake</td>
</tr>
</tbody>
</table>

2.5. Geoaccumulation Index ($I_{geo}$)

The $I_{geo}$ used to evaluate the accumulation of HMs in the soil is calculated as follows [30]:

$$ I_{geo} = \log_2 \left( \frac{C_i}{S_i} \right) $$

where $C_i$ is the measured concentration of HMs (mg/kg) and $S_i$ is the background value of HMs in the soils of Guizhou Province (mg/kg). Factor 1.5 is the correction coefficient to minimize the impact of possible variations in soil caused by changes in background values [31]. According to Müller [31], the $I_{geo}$ can be classified into different grades, as shown in Table 2.
Table 2. Classification criteria for the geoaccumulation index ($I_{\text{geo}}$).

<table>
<thead>
<tr>
<th>$I_{\text{geo}}$ Value</th>
<th>Class</th>
<th>Contamination Situation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{\text{geo}} \leq 0$</td>
<td>0</td>
<td>Unpolluted</td>
</tr>
<tr>
<td>$0 &lt; I_{\text{geo}} &lt; 1$</td>
<td>1</td>
<td>Unpolluted to moderately</td>
</tr>
<tr>
<td>$1 &lt; I_{\text{geo}} &lt; 2$</td>
<td>2</td>
<td>Moderately polluted</td>
</tr>
<tr>
<td>$2 &lt; I_{\text{geo}} &lt; 3$</td>
<td>3</td>
<td>Moderately to heavily</td>
</tr>
<tr>
<td>$3 &lt; I_{\text{geo}} &lt; 4$</td>
<td>4</td>
<td>Heavily polluted</td>
</tr>
<tr>
<td>$4 &lt; I_{\text{geo}} &lt; 5$</td>
<td>5</td>
<td>Heavily to extremely</td>
</tr>
<tr>
<td>$I_{\text{geo}} &gt; 5$</td>
<td>6</td>
<td>Extremely polluted</td>
</tr>
</tbody>
</table>

2.6. Target Hazard Quotient (THQ)

Target hazard quotient (THQ), developed by United States Environmental Protection Agency (USEPA) [32], is widely adopted to evaluate the human body’s risk of ingesting HMs through food crops [2,9], which is calculated as follows [33]:

$$\text{THQ} = \frac{C_{\text{crop}} \times CI \times EF \times ED}{BW \times AT \times RfD}$$ (3)

where $C_{\text{crop}}$ is the metal concentration in edible parts of crop samples (mg/kg); $CI$ is the crop daily intake rate, and the values (the $CI$ of corn for adults is 0.15 kg/person/day and for children, it is 0.1 kg/person/day; the $CI$ of tea is 0.01 kg/person/day) refer to Environmental Protection of China (MEPC) [34]. $BW$ is the body weight, and the $BW$ of adults and children is 56.8 kg and 15.9 kg, respectively; $EF$ is the exposure frequency, 365 days/year; $ED$ is the average exposure duration, 70 years; $AT$ is the average time, 365 $\times$ ED days; and $RfD$ is the chronic reference dose of the toxicant, mg/kg/day. The values are taken from Ministry of Environmental Protection of China (MEPC) [34] and United States Environmental Protection Agency (USEPA) [35]. The calculation parameters and values of the THQ model are listed in Table 3.

Table 3. Reference values of different heavy metals in THQ model.

<table>
<thead>
<tr>
<th>HMs</th>
<th>$RfD$ (mg kg$^{-1}$ d$^{-1}$)</th>
<th>Conversion Rate During Brewing Tea</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.004</td>
<td>19.8%</td>
</tr>
<tr>
<td>Cd</td>
<td>0.001</td>
<td>6.6%</td>
</tr>
<tr>
<td>Hg</td>
<td>0.0002</td>
<td>45.2%</td>
</tr>
<tr>
<td>As</td>
<td>0.003</td>
<td>16.2%</td>
</tr>
<tr>
<td>Cr</td>
<td>0.003</td>
<td>42.0%</td>
</tr>
</tbody>
</table>

2.7. Data Analysis

Microsoft Excel 2013 and SPSS 25.0 were used for descriptive and multivariate statistical analysis of the data. The ArcGIS 10.2, Origin 9.1 and R 6.3.1 packages were used for plotting.

3. Results and Discussion

3.1. HMs in Agricultural Soil

The descriptive statistical data for HMs in soil samples are presented in Table 4. From the average values of soil HMs concentration of different crop types, it can be seen that the HMs concentrations of corn were generally higher, followed by tea and plum. Overall, the mean concentrations of Pb, Cd, Hg, As, and Cr in soil were 39.54 ± 16.56, 0.49 ± 0.49, 0.26 ± 0.33, 25.40 ± 21.34, and 122.50 ± 33.36 mg/kg, respectively. Compared with their corresponding background values, the average growth rate ((Median—Background value)/Background value $\times$ 100%) was ranked as follows: Hg (136%) > Cr (28%) > As (27%)
However, according to the environmental quality standard for soil in China (GB 15618-2018), the average value of HMs did not exceed the risk screening values, indicating that the HMs pollution in the agricultural soil in the study area was controllable. Compared with the classification criteria of selenium contents of soil [36], the statistical results displayed that the concentration of Se (0.90 ± 0.46 mg/kg) in the soil in our study area was relatively high, and the proportion of samples that reached the selenium-enriched (0.4–3 mg/kg) level in the soil was 93%. This was also consistent with previous studies showing that yellow soil is a high-selenium soil in China [37].

### Table 4. Descriptive statistical analysis of HMs concentrations (mg/kg) in agricultural soils in the study area.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Pb (mg/kg)</th>
<th>Cd (mg/kg)</th>
<th>Hg (mg/kg)</th>
<th>As (mg/kg)</th>
<th>Cr (mg/kg)</th>
<th>Se (mg/kg)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tea soil (n = 15)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>17.80–71.30</td>
<td>0.10–0.70</td>
<td>0.11–0.26</td>
<td>10.50–27.40</td>
<td>70.90–203.00</td>
<td>0.59–1.69</td>
<td>4.44–5.51</td>
</tr>
<tr>
<td>Mean</td>
<td>30.59 ± 2.15</td>
<td>0.25 ± 0.19</td>
<td>0.18 ± 0.04</td>
<td>15.97 ± 4.87</td>
<td>113.44 ± 42.95</td>
<td>1.07 ± 0.31</td>
<td>4.83 ± 0.29</td>
</tr>
<tr>
<td><strong>Plum soil (n = 15)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>27.40–44.80</td>
<td>0.13–0.44</td>
<td>0.06–0.12</td>
<td>12.40–18.60</td>
<td>82.50–102.00</td>
<td>0.29–0.79</td>
<td>7.62–8.34</td>
</tr>
<tr>
<td>Mean</td>
<td>35.54 ± 5.06</td>
<td>0.29 ± 0.07</td>
<td>0.08 ± 0.01</td>
<td>15.41 ± 2.07</td>
<td>93.47 ± 5.72</td>
<td>0.52 ± 0.12</td>
<td>8.03 ± 0.25</td>
</tr>
<tr>
<td><strong>Corn soil (n = 55)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Range</td>
<td>18.60–102.00</td>
<td>0.13–2.81</td>
<td>0.09–2.61</td>
<td>7.72–147.00</td>
<td>83.80–200.00</td>
<td>0.24–3.36</td>
<td>4.42–8.26</td>
</tr>
<tr>
<td>Mean</td>
<td>43.07 ± 18.50</td>
<td>0.61 ± 0.57</td>
<td>0.33 ± 0.39</td>
<td>30.70 ± 24.90</td>
<td>132.89 ± 29.62</td>
<td>0.95 ± 0.50</td>
<td>6.32 ± 1.13</td>
</tr>
<tr>
<td><strong>Mean value of agricultural soil</strong></td>
<td>39.54 ± 16.56</td>
<td>0.49 ± 0.49</td>
<td>0.26 ± 0.33</td>
<td>25.40 ± 21.34</td>
<td>122.50 ± 33.36</td>
<td>0.90 ± 0.46</td>
<td>6.36 ± 1.33</td>
</tr>
</tbody>
</table>

| Background reference values | 35.2 | 0.66 | 0.11 | 20 | 95.9 | 0.37 | - |
| Risk screening values | 90 | 0.3 | 1.8 | 40 | 150 | - | - |

* Soil background reference values of HMs in topsoil of Guizhou Province, which were obtained from Ref. [38].
* Risk screening values (5.5 < pH ≤ 6.5) of HMs are taken from Ref. [39].

### 3.2. HMs Contamination in Agricultural Soil

The geoaccumulation index ($I_{geo}$) was calculated to quantitatively evaluate the contamination level in the study area. It can be concluded from Figure 2a that the $I_{geo}$ values were $-0.98–1.53$ for Pb, $-2.74–2.09$ for Cd, $-0.86–4.57$ for Hg, $-1.37–2.88$ for As, and $-0.44–1.08$ for Cr. Additionally, the mean $I_{geo}$ values of the HMs were arranged in the order of Hg (0.78) > Pb (0.07) > As (0.05) > Cd (0.84), and all mean index values of the HMs were lower. The percentages of sites in different pollution classes among the total sample sites were presented in Figure 2b. Obviously, the degree of Hg accumulation was the most obvious, with 5%, 2%, and 1% of the samples reaching pollution classes 3 (moderately to heavily polluted), 4 (heavily polluted), and 5 (heavily to extremely polluted), respectively. Moreover, other HMs samples were concentrated in pollution class 0 (practically unpolluted), class 1 (unpolluted to moderately polluted), and class 2 (moderately polluted), and only the As (3%) and Cd (2%) parts reached class 3. Overall, the contamination of Hg in the study area is worthy of attention. Previous studies have shown that GCCP near the study area, as the only factory in China that used metallic Hg as a catalyst to produce acetic acid from 1971 to 1985, has caused serious Hg contamination to surrounding water and sediments due to the discharge of wastewater, waste gas, and waste residues [12,28]. Therefore, it is reasonable to speculate that the production of this GCCP also leads to regional Hg pollution in the regional soil.
Figure 2. Results of the HMs geoaccumulation index. (a) Boxes represent 25th, 50th (median), and 75th percentiles and whisker minimum and maximum values. Mean values (□); and outliers (○). (b) Percentage of the $I_{\text{geo}}$ at different pollution levels.

3.3. HMs in Crops

The concentrations of HMs in crops directly relate to the health of the local inhabitants. The concentrations of HMs in the crops studied are presented in Table 5. The concentrations of HMs in the three crops varied greatly and the order of the accumulation was Tea > Corn > Plum, which was consistent with the results of previous studies [4]. It is worth noting that the accumulation of Hg and Pb was most obvious in the three crops, whereas Cd and As were not detected in tea, and As was not detected in corn. Referring to the corresponding pollutant limit of each crop, apart from Pb in tea, the maximum value (2.017) exceeded the national standard value (2.0), and the maximum HMs content of each crop was below the national standard value, indicating that the content of HMs in crops in this area was generally at a safe level. Previous studies have shown that the distribution and accumulation of HMs by crops were mainly related to HMs in soil and crop species, physical and chemical soil properties, element solubility, etc. [17,40], among which the concentration and bioavailability of HMs in the soil is the main influencing factor [20]. This is also the reason for the difference in HMs concentration in the three crops in the study area.

Table 5. Descriptive statistical analysis for HM concentrations (mg/kg) in crops in the study area.

<table>
<thead>
<tr>
<th>Crop Type</th>
<th>Pb</th>
<th>Cd</th>
<th>Hg</th>
<th>As</th>
<th>Cr</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tea (n = 15)</td>
<td>Range</td>
<td>1.033–2.017</td>
<td>0.042–0.106</td>
<td>0.056–0.222</td>
<td>0.155–0.311</td>
<td>0.433–1.049</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>1.512 ± 0.265</td>
<td>0.071 ± 0.019</td>
<td>0.109 ± 0.052</td>
<td>0.226 ± 0.048</td>
<td>0.710 ± 0.195</td>
</tr>
<tr>
<td>RV a</td>
<td></td>
<td>2.0</td>
<td>0.5</td>
<td>0.3</td>
<td>0.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Plum (n = 15)</td>
<td>Range</td>
<td>0.005–0.019</td>
<td>Nd-0.001</td>
<td>Nd-0.005</td>
<td>nd</td>
<td>0.005–0.054</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>0.011 ± 0.004</td>
<td>-</td>
<td>0.002 ± 0.002</td>
<td>nd</td>
<td>0.017 ± 0.012</td>
</tr>
<tr>
<td>QPF b</td>
<td></td>
<td>0.1</td>
<td>0.05</td>
<td>0.01</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>Corn (n = 55)</td>
<td>Range</td>
<td>0.043–0.044</td>
<td>0.000–0.077</td>
<td>0.001–0.004</td>
<td>nd</td>
<td>0.002–0.070</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>0.043 ± 0.001</td>
<td>0.008 ± 0.019</td>
<td>0.003 ± 0.001</td>
<td>nd</td>
<td>0.038 ± 0.025</td>
</tr>
</tbody>
</table>

a RV: Reference values of HMs pollution in tea refers to the quantity of pollutants in food, China (GB2762-2017) [41]; limits of chromium, cadmium, mercury, arsenic and fluoride in tea, China (NY 659-2003) [42]; green food-tea, China (NY/T 288-2012) [43]. b QPF: Quantity of pollutants in food, China (GB2762-2017) [41].

3.4. Bioconcentration Factor (BCF)

As shown in Figure 3, the BCF of different elements showed different characteristics in different crops. Cd, Hg, and Se easily migrate from the soil to the crop; in contrast, Cr
showed a poor migration ability. Overall, the BCF average values of HMs of tea in the soil–crop system were higher than those of the other two crops, indicating that HMs most easily accumulated in tea, followed by corn, whereas plum showed the least accumulation. Previous studies indicate that in soil–water conditions, the crops of tea and corn have a higher rate of transport than plum and were more likely to mobilize HMs to edible parts [44]. The tea in particular showed an obvious ability to accumulate HMs [4,9]. Furthermore, other research has shown that the HMs in tea garden soils derived from carbonate rock in Guizhou very clearly accumulates, the BCF of heavy metals in tea decreased in the order of Hg > Cd > Pb > As, and the values of BCF was less than 1, which is basically consistent with the results of the present study [9].

![Figure 3](image)

**Figure 3.** Bioconcentration factors of HMs for different types of crops. (a): tea; (b): Plum; (c): Corn; Mean values (□); and outliers (○).

The migration and transformation processes of HMs in the soil–crop system is complex [20]. Recent research has shown that the concentration of oxides and certain mineral nutrient elements in the soil can affect the absorption and bioavailability of HMs by crops [14,17,45]. A statistical diagram of the correlation between physical and chemical soil properties and HMs bioaccumulation factors is presented in Figure 4. In the soil–tea system, K₂O and MgO were negatively correlated with BCF-Cr and were positively correlated with BCF-Se; SiO₂ was positively correlated with BCF-Pb and BCF-Cr; and Al₂O₃ was negatively correlated with BCF-Pb and BCF-Cr. In the soil–plum system, K₂O was positively correlated with BCF-Cr; BCF-Pb was negatively correlated with SiO₂ and positively correlated with CaO; and pH was negatively correlated with BCF-Cd and BCF-Se. In the soil–corn system, pH was negatively correlated with Na₂O and BCF-Pb; Al₂O₃ was negatively correlated with BCF-Pb; and BCF-Hg and was positively correlated with BCF-Cr. The above results indicated that the BCF-Pb, BCF-Cr, and BCF-Hg of the soil–crop system were affected by pH and clay minerals in the soil, whereas BCF-Cd and BCF-As were basically not affected. At the same time, this research result has also been confirmed by other studies, showing that some oxides and minerals in soil will affect the absorption and accumulation of HMs by crops [14,17].
Figure 4. Cont.
Figure 4. Pearson correlation between transfer factors of HMs and the physicochemical properties of soil for different types of crops (*** denotes significant correlation at $p < 0.001$; ** denotes significant correlation at $p < 0.01$; and * denotes significant correlation at $p < 0.05$).

3.5. Health Risk Assessment of HMs in Edible Part of Crops

Due to the rapid bioaccumulation and long biological half-life, HMs metabolize slowly in the human body and may cause damage to the human body if they accumulate for a long period of time [1,2,9,11]; this has attracted much attention around the world. Many studies have confirmed that food is the main source of people’s exposure to HMs [1,2,46], and continued exposure to HMs, even at low concentration levels, can cause HMs to accumulate in vital organs and pose long-term threats to human health [47]. To consider the health risks to local residents from the ingestion of crops, we calculated the target hazard quotient ($THQ$) of corn for adults and children and tea for adults, and the results are shown in Figure 5. The $THQ$ values of Pb, Cd, Hg, and Cr in corn for adults and children were all less than 1, and the mean values were arranged in the order of Hg > Pb > Cr > Cd, indicating that the health risk to residents who consume HMs in corn was very low, but children were at higher risk than adults (Figure 5a). However, corn is not the staple food of residents and is only the second largest food crop in the local area. Therefore, this study only showed that the HMs ingested by residents only from corn were safe. As shown in Figure 5b, the order of the risk of adults ingesting HMs by drinking tea was Hg (0.041) > As (0.020) > Pb (0.014) > Cd (0.001) > Cr (0.00003); this shows that the intake of Hg and As are the main factors that constitute the risk from drinking tea in the study area. In general, there is a low health risk for residents in the study area ingesting HMs from corn kernels and drinking tea. These results provide a scientific basis for future local research on the health risks of the dietary intake of HMs.
within the BH Reservoir Basin, which is a carbonate area in western China, the concentrations of HMs (Pb, Cd, Hg, As, Cr, and Se) in farmland soil and associated crop (tea, plum, and corn) samples were determined. The results illustrated that the mean concentrations of Pb, Cd, Hg, As, and Cr in the soil were 39.54 ± 16.56, 0.49 ± 0.49, 0.26 ± 0.33, 25.40 ± 21.34, and 122.50 ± 33.36 mg/kg, respectively. The average concentrations of HMs in the crops were generally low, and none of them exceeded the corresponding pollutant limit. Considering the bioaccumulation factors (BCFs) of metals from soil to crops, Cd, Hg, and Se showed higher BCF values than the other metals, and HMs accumulated more easily in tea, followed by corn and plum. The results of the correlation analysis demonstrated that the BCF-Pb, BCF-Cr, and BCF-Hg of the soil–crop system were affected by macro-oxidation in the soil and that the soil pH, K$_2$O, Fe$_2$O$_3$, and Al$_2$O$_3$ were negatively correlated with BCFs in different crop-planting systems. All mean $I_{geo}$ index values of the HMs were lower than 1, and the order was Hg (0.78) > Cr (0.36) > Pb (0.07) > As (0.05) > Cd (−0.84). Moreover, the degree of Hg accumulation was the most evident, with 5%, 2%, and 1% of the samples reaching pollution levels that were moderately to heavily polluted, heavily polluted and heavily to extremely polluted, respectively. The human health risk assessment showed that the THQ values of all HMs were lower than 1, indicating that the health risk to residents who consume HMs from corn and tea is very low.

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![Figure 5. Results of the target hazard quotients: (a) the THQ assessment of corn consumption; and (b) the THQ assessment of drinking tea.](image-url)
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