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Vertical Distributions and Bioavailabilities of Heavy Metals in Soil in An-Tea Plantations in Qimen County, China

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Abstract: Heavy metals mainly enter tea from the soil. In this study, stratified soil samples were collected, at a depth of 0–60 cm, using a soil drill in An-tea plantations. Speciation of As, Cd, Cr, Cu, Ni, Pb, and Zn was determined using the European Community Bureau of Reference sequential extraction method, and the heavy metal concentrations in the extracts were determined by inductively coupled plasma−mass spectrometry. Compared with other soil layers, the mean Cd, Cu, Pb, and Zn concentrations were highest in the 0–20 cm layer, the Ni concentrations were highest in the 20–40 cm layer, and the As and Cr concentrations were highest in the 40–60 cm layer. The mean contributions of the non-residual fractions, including the acid-soluble, reducible, and oxidizable fractions, to the total concentrations were higher than those of the residual fraction for Cr, Cu, and Ni at all depths in soil from a flat area, as well as for Cd and Zn at all depths in soil from a sloping area. The contributions of non-residual fractions to the total As and Pb concentrations were higher than those of the residual fraction in soil from a depth of 0–20 cm from the flat area and soil from a depth of 20–60 cm from the sloping area. The total heavy metal concentrations correlated well with the acid-soluble fraction and reducible fraction concentrations in soil from 0–40 cm.

Keywords: heavy metal fraction; bioavailability; inductively coupled plasma mass spectrometry; An-tea; non-residual fraction

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1. Introduction

There are various elements in tea, and these can have either positive or negative effects on human health. Some macroelements, including K, Na, and P, and micronutrients that are required in trace quantities are present in tea and beneficial for human health. Regular consumption of tea contributes to the daily dietary requirements of some of these elements [1]. However, heavy metals (HMs), such as As, Cd, Cr, and Pb, are biologically nonessential and can be toxic [2]. Some HMs can increase the risks of skin and lung cancer, urinary tract disorders, cardiovascular diseases, neurotoxic effects, and diabetes [3,4].

Many studies have shown that the total HM concentration can be used to evaluate the pollution status of an environmental medium [5]. However, the total HM concentration does not provide information on the bioavailabilities, mobilities, and toxicities of the HMs in the medium [6]. The bioavailability of a HM is strongly related to its ability to migrate, and it is controlled, in a complicated way, by the degree to which the HM is sorbed to the medium [7]. Because of various physical, chemical, and biological processes, HMs in soil are present as different species that are defined as exchangeable, associated with Fe/Mn oxides, organic matter (OM), and residual [8,9]. The bioavailability of HMs to plants decreases in the order exchangeable fraction >Fe/Mn oxide-associated fraction >OM-bound oxidizable fraction; the residual fraction is not bioavailable [10]. The exchangeable fraction can sorb to soil particles through adsorption or as a precipitate, and various biological and chemical mechanisms can cause this fraction to become mobile in a soil solution [11]. Mobile HMs can be absorbed by plants and enter the food chain [12,13]. Therefore, it is important to investigate the concentrations of HMs in the labile fractions of soil in tea plantations [14,15].

Recent research has focused on method development for determining the bioavailability of HMs. Single extraction and sequential extraction methods are currently the most commonly used methods to extract HMs from soil. The single extraction method, which is simple and effective, involves extracting HMs using chemicals, such as dilute nitric acid and dilute hydrochloric acid, to assess HM pollution. The European Community Bureau of Reference sequential extraction method gives stable, reproducible, and precise results and has been widely used [16]. The amounts of HMs in different fractions in soil can be determined using a modified European Community Bureau of Reference sequential extraction method [17].

An-tea, or "holy tea", is considered to have medicinal properties and a famous traditional tea grown in the mountains of south Anhui Province, China. An-tea has "Protected Geographical Product" status in China [18]. It is a semi-fermented tea that is wrapped in the leaves of *Indocalamus* and pressed into a bamboo basket. Recent research has shown that soil in tea plantations can contain relatively high concentrations of HMs, which can affect the yield and quality of the tea. Some Al species in tea infusions are apparently readily absorbed by humans, and the bioavailability of Al is dependent on its speciation [19]. A study in a 15-year-old tea plantation in Anxi, China, found that the concentrations of acid-extractable fractions of Pb and Sr in topsoil were positively correlated with their concentrations in new leaves (Pb), as well as both new and old leaves (Sr) [20]. Therefore, HMs in active fractions may be transferred from soil into tea leaves. However, most previous studies have only looked at HMs in surface soil (0–20 cm deep) and not in deeper soil. Because HMs in soil can be absorbed by the fine roots of a tea plant, the vertical distribution of fine roots will affect the availability of HMs to the plant. Approximately 47% of the fine roots of tea plants are located in the upper 45 cm of soil, and lateral roots typically reach depths of no more than 1 m [21,22]. Therefore, it is important to investigate the vertical distributions and bioavailabilities of HMs in soil in tea plantations.

The objectives of this study were: (1) to determine the vertical distributions of HM fractions in soil; (2) to identify relationships between the non-residual HM concentrations at different soil depths and HM concentrations in tea leaves; and (3) to assess the vertical variations in the bioavailabilities of HMs.

2. Materials and Methods

2.1. Study Area

The study area (Figure 1) was located at 29°41′ N, 117°30′ E in a mountainous area in South China with a humid subtropical monsoon climate. The mean annual precipitation in the study area is >1600 mm, mean annual temperature is 15.6 °C, and frost-free period is 235 days. The study area has yellow soil, and the parent materials are phyllite, phyllitic siltstone, slate, shale, and other weathered residues and slope sediment. Red soil has only developed on the steep slopes of mountains at low to moderate elevations. The mean pH of the soil samples was 4.52, and the mean OM content was 31.82 $g \cdot mg^{-1}$.

2.2. Collection and Processing of Samples

Samples were collected from two randomly selected An-tea plantations in Luxi Village, Qimen County, Anhui Province, China. One tea plantation was located on sloping land (plantation S), and the other was located on flat land (plantation F). Three sampling lines were established in each plantation. The lines in plantation S were 5 m apart and labeled, with increasing distance from a river in the area, as S1, S2, and S3. The lines in plantation F were 10 m apart, in terms of elevation, and labeled, from the lowest to the highest point, as S4, S5, and S6. Three soil sampling points were established along each sampling line, and soil samples were collected from depths of 0–20, 20–40, and 40–60 cm at each sampling point. Each sample was placed in a 150 × 90 mm polyethylene bag, which was then sealed. Fresh tea leaves were randomly picked from tea plants close to each sampling point, at the same time as the soil samples were collected, and one bag of leaves from around each sampling point was taken for analysis. After drying the soil samples in air, stones, roots, and other debris were removed, and the soil was ground and passed through a 1 mm sieve. One quarter of each soil sample was retained for testing. The fresh leaf samples were dried at 60 °C for 24 h before analysis.

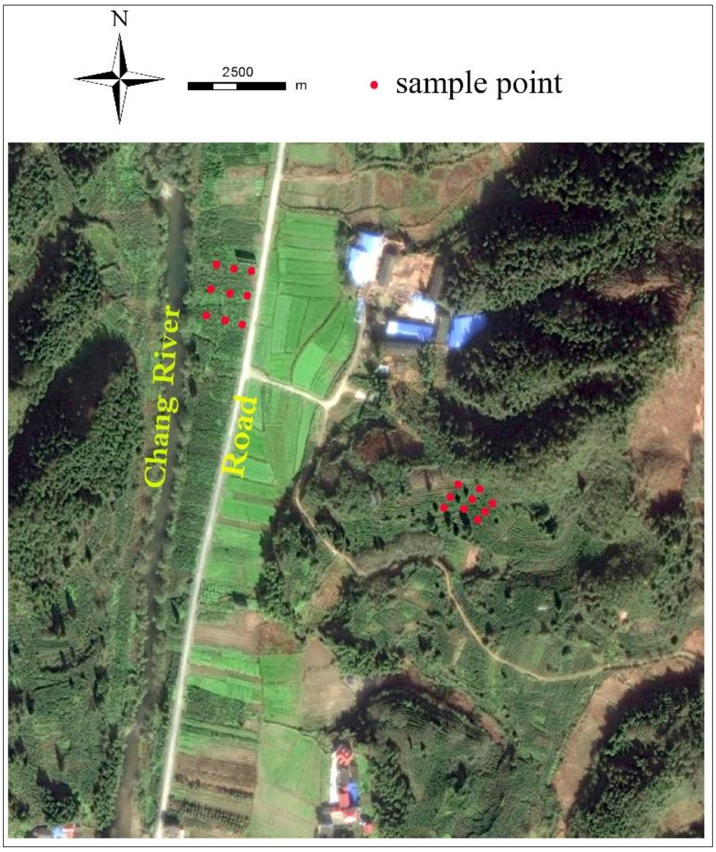


Figure 1. Map of the study area with the sampling points marked.

2.3. *Standard Substances for Soil Composition Analysis*

Four representative soil types for standard soil composition analysis were present in the study area: limestone soil (GBW07404), yellow earth (GBW07405), yellow-brown earth (GBW07406), and latosol (GBW07407) [23]. Yellow-brown earth (GBW07406) was chosen to calculate the recovery rate of HMs in this experiment.

2.4. *Sample Analysis*

The total HM concentrations were determined by digesting samples in a microwave digestion instrument (PreeKem Scientific Instruments Co., Ltd., Shanghai, China) and then analyzing the digested samples by inductively coupled plasma mass spectrometry (ICP-MS). For the soil samples, 500.0 mg of soil was mixed with 5 mL of HNO_3 and 1 mL of HF; GBW07406 was treated in the same way. For the leaf samples, 100.0 mg of leaves was mixed with 5 mL of HNO_3. Digestion was performed using set temperature and pressure conditions (Table 1). The ventilation system was opened after the digestion instrument had cooled. The digestion tank was placed on a temperature-controlled electric heating plate, at 150 °C, and the samples were evaporated to near dryness. The residue was transferred to a 50 mL volumetric flask, and 2% HNO_3 was added to make the solution up to the mark. Blank tests were also carried out.

Table 1. Microwave digestion conditions.

Steps	T/°C	Pressure/MPa	t/min
1	150	15	3
2	180	25	3
3	200	30	3
4	220	35	15

Speciation was achieved by extracting HMs from the samples, using the soil and sediment sequential extraction procedure (Figure 2), for the speciation of 13 trace elements, as specified in the Chinese standard GB/T 25282-2010 [24], which is an improved version of the European Community Bureau of Reference continuous extraction method. The pH of the soil was determined using a pH meter, and the OM content was determined using the potassium dichromate volumetric method.

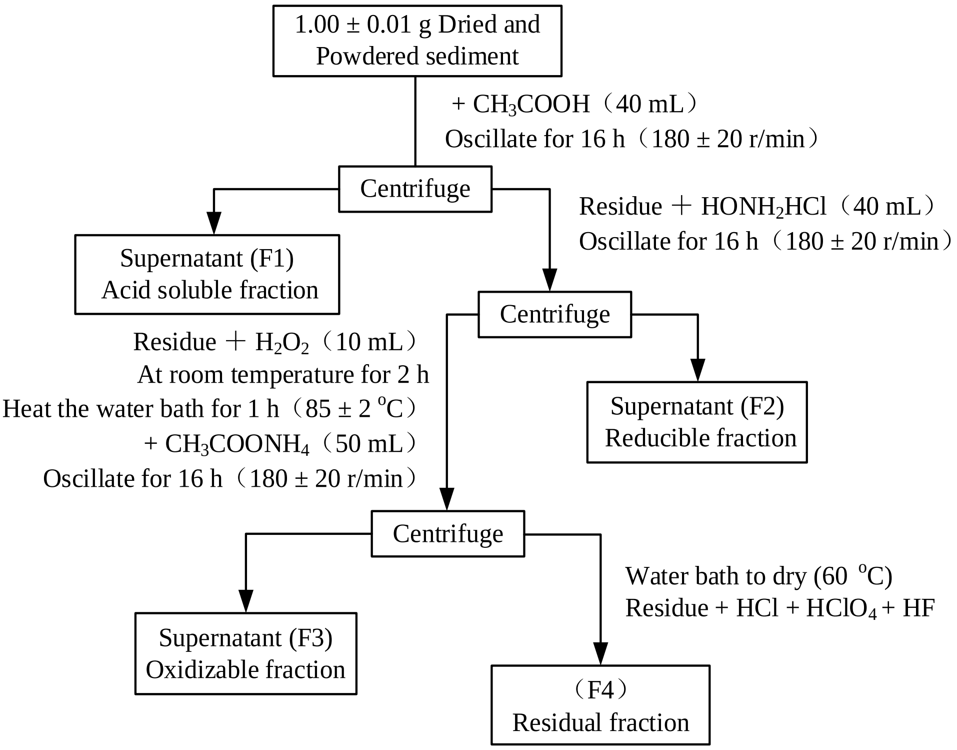


Figure 2. Sequential extraction process based on the European Community Bureau of Reference method.

2.5. Determination of HMs by ICP-MS

The concentrations of the HMs As, Cd, Cr, Cu, Ni, Pb, and Zn in the sample extracts were determined using an inductively coupled plasma mass spectrometer (ICAP-Q; Thermo Fisher Scientific, Waltham, MA, USA). The preparation of standard solution was using the similar method with [23]. The operational parameters are given in Table 2.

Table 2. Operational parameters for ICP−MS.

Working Parameters	Conditions	Working Parameters	Conditions	Working Parameters	Conditions
RF power	1500 W	Cooling water flow rate	3.73 L/min	Flow rate of cooling gas	13 L/min
Flux of atomize	1 L/min	Vacuum sampling depth	10 mm	Vacuum	3.078×10^{-7} MPa
Assistant gas flow	0.8 L/min	Peristaltic pump speed	40 RPM	Times of repetition	3

2.6. Data Processing and Statistical Analyses

The bioavailability of a HM in soil is the proportion of the total HM concentration in soil that is readily, or relatively readily, available to organisms. The HM fraction soluble in a slightly acidic solution (F1) and reducible HM fraction (F2) are readily, or relatively readily, available to organisms. The bioavailability of a HM in soil can be described using the K value. The higher the K value, the more toxic the HM will be to tea plants. The following equation can be used to calculate K:

$$K = \frac{\mathrm{F1} + \mathrm{F2}}{\mathrm{F1} + \mathrm{F2} + \mathrm{F3} + \mathrm{F4}} \times 100\%, \tag{1}$$

Each soil or tea sample was analyzed in triplicate, and the data presented are the means of the values for the triplicate samples on a dry weight basis. Excel 2016 (Microsoft, Redmond, WA, USA), SPSS 20.0 (IBM, Armonk, NY, USA), and Origin 9.0 (OriginLab, Northampton, MA, USA) were used to analyze and plot the data. One-factor analysis of variance was performed using a significance level of 0.05. Fisher least significant difference post hoc tests were also performed.

3. Results

3.1. HM Distributions in Tea Plantation Soil

The total concentrations of the seven HMs in the soil samples are summarized in Table 3. The concentrations at all soil depths tended to decrease, in the order Zn > Cr > Pb > As > Cu > Ni > Cd. The Zn concentrations were significantly higher than the Cr concentrations ($p < 0.05$). The Cr concentrations were significantly higher than the As, Cu, Ni, and Pb concentrations ($p < 0.05$). The As, Cu, Ni, and Pb concentrations were significantly higher than the Cd concentrations ($p < 0.05$). There were no significant differences between the Cu, Ni, and Pb concentrations. The HM concentrations were compared with the limits defined for soil at pH $\leq$ 5.5 in the Chinese Soil Environmental Quality Agricultural Land Soil Pollution Risk Control Standards (trial) [25]. The As, Cd, and Zn concentrations in 11.11%, 27.78%, and 7.41% of the soil samples, respectively, were higher than the relevant limits. The concentrations of the other HMs were lower than the relevant limits in the samples from all depths.

Table 3. Heavy metal concentrations, pH values, and total organic carbon (TOC) contents of soil samples from different depths in An-tea plantations.

Item	Depth	Zn (mg·kg^{-1})	Cr (mg·kg^{-1})	Pb (mg·kg^{-1})	As (mg·kg^{-1})	Cu (mg·kg^{-1})	Ni (mg·kg^{-1})	Cd (mg·kg^{-1})	pH	TOC (g·kg^{-1})
Min−Max	0–20 cm	47.02–261.13	28.59–91.78	11.48–63.12	11.93–48.31	9.16–29.90	6.99–22.79	0.10–0.39	3.07–5.90	17.05–50.41
	20–40 cm	51.36–210.34	28.25–88.18	10.81–56.83	10.17–55.50	9.89–26.78	10.87–28.09	0.08–0.31	3.14–5.74	10.59–50.22
	40–60 cm	51.51–316.67	22.29–89.15	10.35–53.14	11.07–44.68	9.40–37.76	9.50–24.09	0.04–0.37	3.95–5.45	17.45–58.38
Mean ± S	0–20 cm	107.97 ± 52.3 $_{\mathrm{a,A}}$	47.60 ± 14.4 $_{\mathrm{a,B}}$	29.32 ± 13.1 $_{\mathrm{a,C}}$	24.20 ± 10.8 $_{\mathrm{a,C}}$	18.10 ± 2.8 $_{\mathrm{a,C}}$	14.74 ± 4.0 $_{\mathrm{a,C}}$	0.23 ± 0.2 $_{\mathrm{a,D}}$	4.64 ± 0.9 $_{\mathrm{a}}$	32.75 ± 12.8 $_{\mathrm{a}}$
	20–40 cm	100.61 ± 40.0 $_{\mathrm{a,A}}$	52.86 ± 15.2 $_{\mathrm{a,B}}$	28.79 ± 11.4 $_{\mathrm{a,C}}$	24.00 ± 11.8 $_{\mathrm{a,C}}$	17.93 ± 4.8 $_{\mathrm{a,C}}$	17.22 ± 4.9 $_{\mathrm{a,b,C}}$	0.21 ± 0.2 $_{\mathrm{a,D}}$	4.46 ± 1.3 $_{\mathrm{a}}$	29.15 ± 14.6 $_{\mathrm{a}}$
	40–60 cm	104.03 ± 57.1 $_{\mathrm{a,A}}$	53.79 ± 19.5 $_{\mathrm{a,B}}$	28.41 ± 11.3 $_{\mathrm{a,C}}$	24.34 ± 9.2 $_{\mathrm{a,C}}$	17.88 ± 7.3 $_{\mathrm{a,C}}$	15.77 ± 4.3 $_{\mathrm{b,C}}$	0.23 ± 0.2 $_{\mathrm{a,D}}$	4.40 ± 0.7 $_{\mathrm{a}}$	38.48 ± 14.7 $_{\mathrm{a}}$
Limit Standard * [25,26]		200.00	150.00	70.00	40.00	50.00	60.00	0.30	-	-

Notes: Different lower-case letters in the same column and different capital letters in the same row indicate significant differences at $p < 0.05$, according to least significant difference tests. * The standard value is the risk screening value at pH $\leq$ 5.5.

The HM concentrations found in the soil samples in the present study and soil from tea plantations in other areas are shown in Table 4.

Table 4. Heavy metal concentrations (mg·kg^{-1}) in soil from An-tea plantations in the present study and from plantations in other areas from previous studies.

Region	Zn	Cr	Pb	As	Cu	Ni	Cd
Qimen *	104.20	51.41	28.84	24.18	17.97	15.91	0.22
Anxi [26]	76.90	15.80	49.20	3.99	15.70	6.50	0.04
Fuzhou [26]	151.30	31.70	73.50	5.66	86.00	17.80	0.16
Suzhou [27]	198.13	82.58	83.96	5.57	19.72	29.15	0.12
Nanjing [28]	62.80	83.74	34.65	ND	17.16	31.71	ND

Notes: ND, not detected. * The samples were collected in Luxi Village, Qimen County, Anhui Province, China.

The Zn concentrations were higher and Cd concentrations were lower in the soil samples from the tea plantations in Luxi than in soil from other tea plantations. The mean As and Cd concentrations were markedly higher in the soil samples from the An-tea plantations in Luxi than in soil from tea plantations in Anxi County [26], Fuzhou [26], and Suzhou [27] in China. The Zn concentrations were higher in the soil samples from the An-tea plantations in Luxi than in soil from tea plantations in Nanjing [28] and Anxi County [26] in China. The Cr, Cu, Ni, and Pb concentrations were lower in the soil samples from the An-tea plantations in Luxi than in soil samples from the other tea plantations.

The Cd, Cu, Pb, and Zn concentrations were higher in the soil from a depth of 0–20 cm than in deeper soil, but the Cr and Ni concentrations were lower in the soil from a depth of 0–20 cm than in deeper soil. The As, Cd, and Zn concentrations were lower and Ni concentrations were higher in the soil from a depth of 20–40 cm than in soil from other depths. The As concentrations were higher in the soil from a depth of 40–60 cm than in soil from other depths. The Cu and Pb concentrations decreased but Cr concentration increased as the soil depth increased. There were no significant differences between the concentrations of the seven HMs in the different soil layers.

The soil samples from the An-tea plantations were very acidic (mean pH: 4.47, pH range: 3.07–5.90). The OM contents were high (mean: 31.82 g·kg^{-1}, range: 8.93–58.38 g·kg^{-1}).

3.2. Vertical Distributions of the HM Fractions

3.2.1. Chromium

The Cr concentrations in the slightly acid-soluble and oxidizable fractions were higher for the S2 samples from a depth of 0–60 cm than for the S1 and S3 samples from the same depth (Figure S1). The Cr concentration in the F1 fraction of the S3 sample (distant the river) increased as the soil depth increased. By contrast, the Cr concentrations in the F1 and F3 fractions of the samples from the other sampling lines decreased as the soil depth increased. For samples from the S1 line, the Cr concentration in the F2 fraction was higher in soil from a depth of 40–60 cm than in soil from other depths. For samples from the S2 line, the Cr concentration in the F2 fraction was higher in soil from a depth of 20–40 cm than in samples from other depths. For samples from the S3 line, the Cr concentration in the F2 fraction was lower in soil from a depth of 0–20 cm than in samples from other depths. The Cr concentration in the residual fraction was much higher in soil from a depth of 20–60 cm from sampling line S1 than for soil from a depth of 20–60 cm from the other sampling lines. The Cr concentrations in the F1 fractions were higher for the S4 and S6 samples from a depth of 20–40 cm than for the sample from a depth of 20–40 cm in the flat area (sampling lines S1–S3) (Figure S2). The Cr concentrations in the F1 fractions of the samples from sampling line S5 decreased as the soil depth increased. The Cr concentrations in the F2 and F3 fractions of the samples from sampling lines S5 and S6 decreased as the soil depth increased. The Cr concentrations in the F4 fractions were much lower for samples from the entire depth profile (0–60 cm) from line S4 than for the different layers of soil from the other lines.

3.2.2. Cadmium

The Cd concentrations in the F1 fractions were higher in the soil samples from a depth of 0–60 cm in the flat area than in the samples from sampling lines S1 and S3 (Figure S3). The Cd concentrations in the F1 fractions of the soil samples from the three sampling lines in the flat area decreased as the soil depth increased. The Cd concentrations in the F2 fractions were higher for all of the soil layers (0–20, 20–40, and 40–60 cm) from sampling line S2 than for the same soil layers from the other lines. There was little variation among the Cd concentrations in the different soil layers from the three sampling lines. The Cd concentrations in the F3 fractions of the samples from S1 (close to the river) and S3 (distant from the river) decreased as the soil depth increased. The Cd concentration was higher in the F3 fraction from a depth of 20–40 cm at S2 (sampling line at the middle distance from the river) than in the F3 fractions of the S2 samples from other depths. The residual Cd concentration was highest in the soil from a depth of 0–20 cm from sampling line S3. The residual Cd concentration was lowest in the soil from a depth of 20–60 cm from sampling line S2. The Cd concentration in the F1 fraction of the soil from a depth of 0–20 cm from sampling line S4 was 0.19 mg kg^{-1} (Figure S4), which was higher than the Cd concentrations in the F1 fractions of the soil from this depth from the other sampling lines. The Cd concentrations in the F2 fractions were higher for soil from all depths (i.e., 0–60 cm deep) from sampling line S4 than for soil from all depths from sampling lines S5 and S6. For the S4 and S6 soil samples, the Cd concentrations in the F2 fractions decreased as the soil depth increased. The Cd concentrations in the F3 fractions decreased as the soil depth for the S4 samples remained almost constant as the soil depth increased for the S5 samples, which first increased and then decreased as the soil depth increased for the S6 samples. For the F4 fraction, the Cd concentration was markedly higher in soil from a depth of 0–60 cm from sampling line S4 than in soil from the same depth from the other sampling lines.

3.2.3. Nickel

The Ni concentrations in the F1 fractions of the samples from sampling line S1 did not vary markedly as the soil depth increased. By contrast, the Ni concentrations in the F1 fractions of the samples from sampling lines S2 and S3 decreased as the soil depth increased (Figure S5). The Ni concentrations were markedly higher in the F1 fractions of the samples from line S1 than in the F1 fractions of the samples from lines S2 and S3. The Ni concentrations in the F2 fractions of the samples from lines S1 and S3 increased as the soil depth increased, but the Ni concentration was higher in the F2 fraction of the soil from a depth of 20–40 cm from sampling line S2 than for the samples from other depths. For the F3 fractions, the Ni concentrations were higher in soil from depths of 0–20 and 40–60 cm from sampling line S1 than for most of the other samples. The Ni concentration in the F3 fraction of the soil from a depth of 20–40 cm from sampling line S2 sample was even higher. The Ni concentrations in the F4 fractions of the soil from 0–20 cm from the three sampling lines in the flat area were similar, and the Ni concentrations in the F4 fractions of the soil from a depth of 20–60 cm decreased, in the order S1 > S2 > S3.

The Ni concentrations in the F3 fractions of the soil from 0–60 cm from the sloping area decreased, in the order S5 > S4 > S6 (Figure S6). The Ni concentrations in the F3 fractions in the samples from the three sampling lines in the sloping area did not vary markedly. The Ni concentrations in the F4 fractions of the samples from lines S4 and S5 decreased as the soil depth increased. By contrast, the Ni concentrations in the F4 fractions of the samples from line S6 increased as the soil depth increased. The Ni concentration was higher in the F4 fraction of the soil from 20–60 cm at S6 than the Ni concentrations in soil from the same depth at the other sampling lines in the sloping area.

3.2.4. Zinc

The Zn concentration in the F1 extract of the soil from a depth of 0–20 cm at S3 (distant from the river) was markedly higher than the Zn concentrations in the F1 extracts of soil from the same depth from the other sampling lines (Figure S7). In the F1 fractions of the samples from all three lines in the flat area, the Zn concentration decreased as the soil depth increased. The Zn concentrations in the F2 fractions of soil from a depth of 0–20 cm were similar for the three sampling lines in the flat area. The Zn concentration was higher in the F2 fraction of the soil from a depth of 20–40 cm from S1 than in the F2 fraction of the soil from the same depth from the other sampling lines in the flat area. The Zn concentration was higher in the F2 fraction of the soil from a depth of 40–60 cm from S3 than in the F2 fraction of the soil from the same depth from the other sampling lines in the flat area. As the soil depth increased, the Zn concentrations in the F3 and F4 fractions of the S1 and S3 samples decreased and Zn concentrations in the F3 and F4 fractions of the S2 samples increased.

The Zn concentration in the F1 fraction of the soil from 0–20 cm from S5 was 53.89 mg kg^{-1}, which was markedly higher than the Zn concentrations in the F1 fractions of the soil from 0–20 cm from the other sampling lines in the sloping area (Figure S8). The Zn concentrations in the F1 fractions of the S4 and S6 samples did not markedly change as the soil depth increased. In the three sampling lines in the sloping area, the highest concentrations of F2 were observed at S4 for the 0–20 cm layer and the 20–40 cm layer, as well as at S6 for the 40–60 cm layer. The Zn concentrations in the F3 fractions were higher for the S5 samples from all soil depths than for the samples from the other sampling lines in the sloping area. The highest concentration (61.26 mg kg^{-1}) was observed in soil from a depth of 20–40 cm from S5. The Zn concentrations in the samples from S4 and S6 decreased as the soil depth increased. The Zn concentration in the F4 fraction of the soil from a depth of 20–40 cm from S4 (667.84 mg kg^{-1}) was markedly higher than the concentrations at other depths; however, the Zn concentrations in the samples from the lines in the sloping areas varied little as the soil depth increased.

3.2.5. Arsenic

The As concentrations in the F1 fractions of the S3 samples obtained at depths of 0–20 and 40–60 cm were 0.06 and 0.01 mg kg^{-1}, respectively (Figure S9); As was not detected in the F1 fraction of the other samples. The As concentrations in the F2 fractions of the S1 samples increased as the soil depth increased. By contrast, the As concentrations in the F1 fractions of the S2 samples increased and then decreased as the soil depth increased, and the As concentrations in the S3 samples decreased and then increased as the soil depth increased. The As concentrations in the F3 fractions of the S1 and S2 samples decreased as the soil depth increased. The As concentration was lower in the S3 sample from a depth of 20–40 cm than in the other S3 samples. In the F4 fractions of the S1 and S3 samples, the As concentrations decreased as the soil depth increased. The As concentration was higher in the F4 fraction of the S2 sample from a depth of 20–40 cm than in the F4 fractions of the other samples from the flat area.

The As concentrations in the F1 fractions of the S4 and S6 samples from a depth of 0–20 cm were relatively low (Figure S10). The As concentrations in the F2 fractions of the soil from a depth of 0–60 cm decreased, in the order S5 > S4 > S6. The As concentrations in the F3 fractions of the S5 and S6 samples decreased as the soil depth increased, but the As concentrations in the F3 fractions of the S4 samples increased as the soil depth increased. The As concentrations were higher in the F4 fractions of the S4 samples from a depth of 0–60 cm than in the F4 fractions of samples from the same depth, collected at other lines in the sloping area. The As concentrations in the F4 fractions of the samples from the sloping area decreased as the soil depth increased.

3.2.6. Lead

The Pb concentrations in the F1 and F3 fractions of the samples from the flat area decreased as the soil depth increased (Figure S11). The Pb concentrations in the F2 fractions of the soil from a depth of 0–20 cm in the flat area were similar. In the F2 fractions of the S2 sample from a depth of 20–40 cm and S1 sample from a depth of 40–60 cm, the Pb concentrations were higher than those in the F2 fractions of the other samples from the flat area. The Pb concentrations in the F4 fractions of the S1 and S3 samples decreased as the soil depth increased, while the Pb concentrations in the F4 fractions of the S2 samples increased as the soil depth increased.

The Pb concentrations in the F1 and F2 fractions were higher in the S5 sample from the surface than in the samples from deeper soil. In the F1 and F2 fractions of the S5 sample from a depth of 0–20 cm, the Pb concentrations were 5.37 and 12.09 mg kg^{-1}, respectively (Figure S12). The Pb concentrations in the F1 and F2 fractions of the S4 and S6 samples did not vary markedly as the soil depth increased. The Pb concentrations in the F4 fractions of the S4 and S5 samples decreased as the soil depth increased. The highest Pb concentration in the F3 fractions of the S6 samples was found in soil from a depth of 20–40 cm. The Pb concentrations in the F4 fractions of the S4 samples decreased as the soil depth increased. The Pb concentrations in the F4 fractions of the S5 and S6 samples did not vary markedly as the soil depth increased.

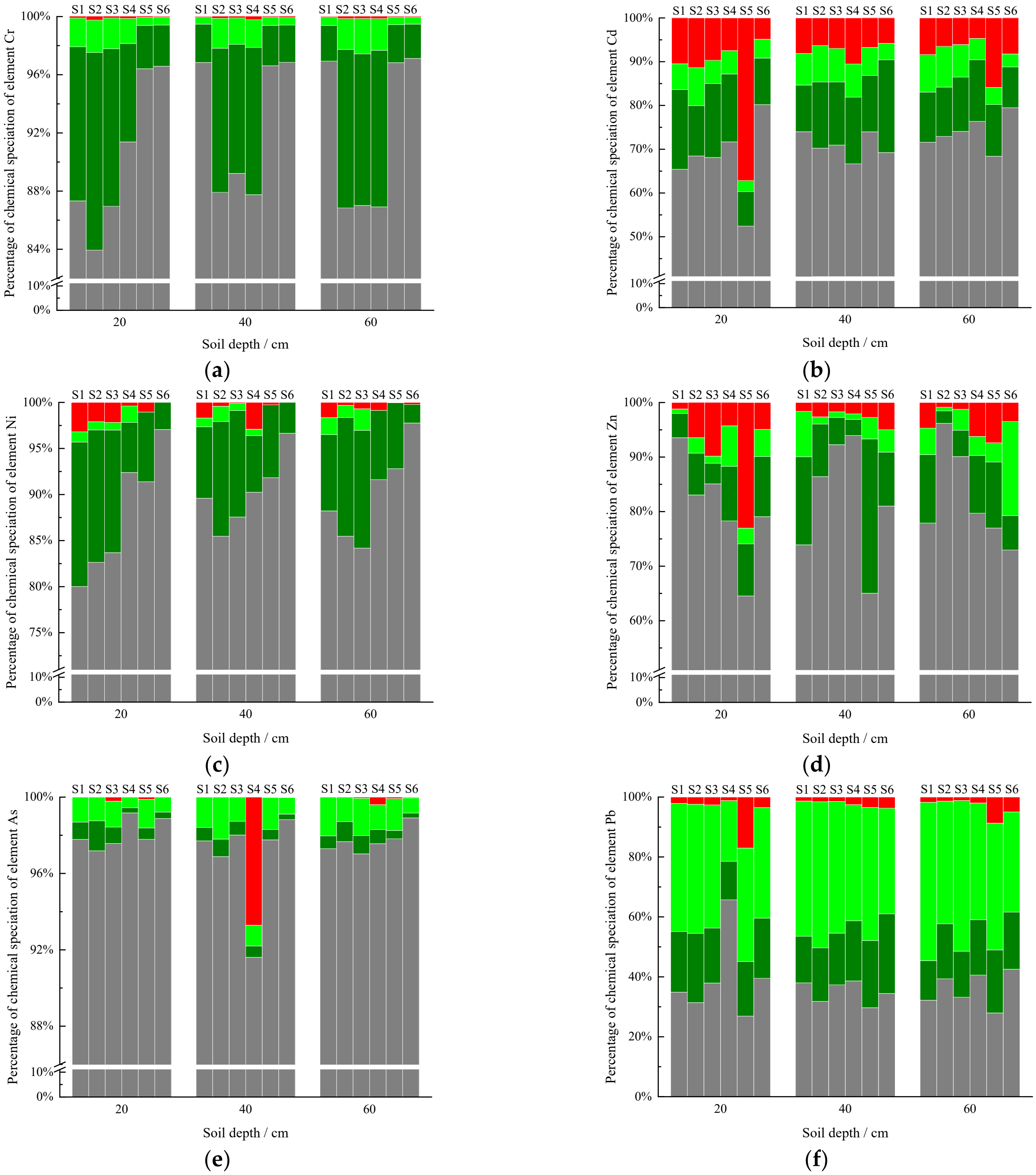
3.2.7. Copper

The Cu concentrations found in the samples from the flat area are shown in Figure S13. The Cu concentrations in the F1 and F2 fractions of the samples from the flat area decreased as the soil depth increased. The Cu concentration was clearly higher in the F1 fraction of the S3 sample from a depth of 0–20 cm (0.68 mg kg^{-1}) than in the F1 fractions of S3 samples of deeper soil. In the F3 fractions, the Cu concentrations over the full soil-depth profile decreased in the order S2 > S1 > S3. The Cu concentrations were higher in the F2 fractions of the S1 and S2 samples from a depth of 20–40 cm than in the other S1 and S2 samples. In the F2 fraction of the deep S3 sample, the Cu concentration was lower than in the other S3 samples. For all sampling lines in the flat area, the Cu concentrations were higher in the F4 fractions of the samples from a depth of 20–40 cm than in the samples from other soil depths. The Cu concentration was higher in the F4 fraction of the S1 sample from a depth of 0–60 cm than in the F4 fractions of the samples from the same soil depth collected at other sampling lines in the flat area.

The Cu concentrations in the F1, F2, and F3 fractions of the soil samples collected at a depth of 0–60 cm in the sloping area decreased, in the order S5 > S4 > S6 (Figure S14). The Cu concentration was markedly higher in the F4 fraction of the S4 sample collected at a depth of 0–20 cm than in the F4 fractions of the samples from the same depth at other sampling lines in the sloping area. In the F4 fractions of the S4 and S5 samples, the Cu concentrations increased as the soil depth increased. The Cu concentrations in the F4 fractions of the S6 samples decreased as the soil depth increased.

There were marked differences between the vertical distributions of the seven HMs in the soil samples from the two tea plantations (flat and sloping). HMs in the non-residual fractions (F1, F2, and F3) would be available to the tea plants.

The ratios of the non-residual fraction concentration to total concentration (F1 + F2 + F3 + F4) for Cr, Cu, and Ni for the full soil depth (0–60 cm) in samples from the flat area were all high (Figure 3). These ratios were also high for Cd and Zn, for the full soil depth in samples from the sloping area. For As and Pb, these ratios were high for samples from depths of 0–20 cm in the flat area and 20–60 cm in the sloping area. HM speciation is related to the HM sources, environment, and interactions with other substances. The differences we found may have been caused by the soil in the flat and sloping areas having different parent materials. Zhang [29] suggested that the parent materials of soil affect HM distribution and accumulation. Therefore, different parent materials could have caused the differences in the HM distributions that were found for the soil samples from the two tea plantations in this study. The soil in the sloping area will have developed from weathered residual parent materials through a series of soil-forming processes. However, the soil in the flat area would have formed from alluvial deposits, and transport and accumulation of river sediment would have controlled the soil characteristics. Previous studies have shown that proximity to a river, fertilization, elevation, slope, and aspect may affect HM concentrations in soil in tea plantations [30,31].

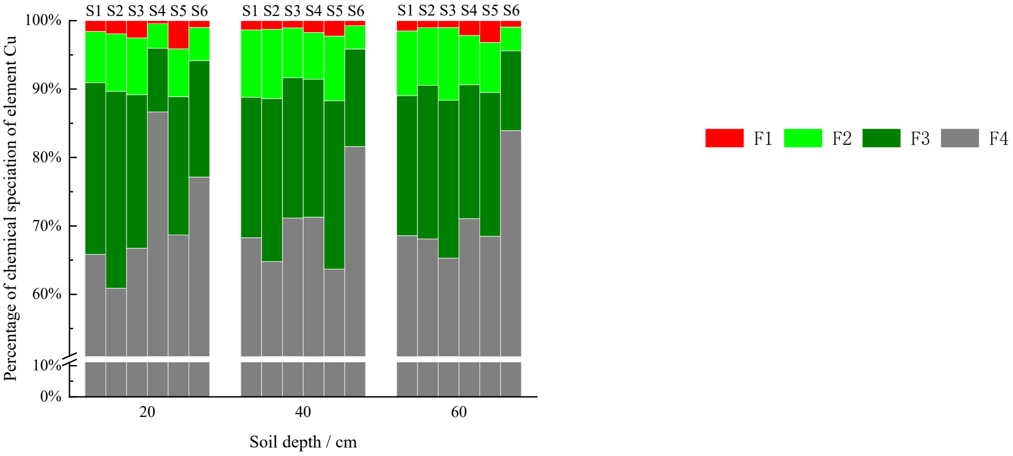


(**a**) (**b**)

(**c**) (**d**)

(**e**) (**f**)

Figure 3. *Cont.*



(g)

Figure 3. Percentage of Heavy metal speciation in the soil samples from the An-tea plantations (**a**) Cu, (**b**) Cd, (**c**) Ni, (**d**) Zn, (**e**) As, (**f**) Pb, and (**g**) Cu.

4. Discussion

4.1. Bioavailabilities of HMs in Tea Plantation Soil

The bioavailability of a HM will strongly affect its toxicity towards organisms. The bioavailability of a HM can be evaluated using indirect toxicity data or concentrations in organisms [32]. Generally, the bioavailability of a HM is evaluated using the ratio between the sum of the soluble and extractable HM concentrations and total HM concentration (the *K* value). The higher the *K* value, the larger the proportion of the HM that can be absorbed and used by a tea plant. In this study, the *K* values for different HMs in the soil samples from the An-tea plantations were markedly different (Table 5). For example, the *K* values were higher for Pb than for the other HMs. The mean *K* value for Pb in the samples from the six sampling lines was 44.43%, and the range was 21.43–54.85%. The mean *K* values for Cd, Cu, and Zn were 15.84% (range: 9.17–39.70%), 9.05% (range: 4.02–11.72%), and 9.05% (range: 1.54–25.92%), respectively. By comparison, the mean *K* values for Ni, As, and Cr were relatively low, at 2.13% (range: 0.02–4.30%), 1.79% (range: 0.56–7.80%), and 1.47% (range: 0.52–2.56%), respectively. The bioavailable concentrations of the seven HMs in the soil samples from the An-tea plantations decreased, in the order Pb > Cd > Cu > Zn > Ni > As > Cr.

Table 5. *K* values (%) for heavy metals in the soil samples from An-tea plantations.

Belt	Depth/cm	Cr	Cd	Ni	Zn	As	Pb	Cu
S1	0–20	2.08 ± 0.35	16.34 ± 3.63	4.30 ± 1.68	1.99 ± 0.13	1.31 ± 0.46	44.84 ± 9.16	9.07 ± 0.60
	20–40	0.52 ± 0.03	15.33 ± 3.80	2.65 ± 0.61	9.96 ± 0.72	1.59 ± 0.33	46.46 ± 7.78	11.19 ± 1.24
	40–60	0.61 ± 0.03	16.95 ± 2.59	3.50 ± 0.44	9.55 ± 0.73	2.03 ± 0.68	54.59 ± 5.01	10.98 ± 0.49
S2	0–20	2.48 ± 0.14	20.04 ± 2.41	2.98 ± 0.82	9.29 ± 0.66	1.24 ± 0.28	45.48 ± 4.36	10.34 ± 0.87
	20–40	2.17 ± 0.42	14.64 ± 2.38	2.07 ± 0.39	3.95 ± 0.53	2.20 ± 0.24	50.30 ± 6.17	11.40 ± 0.26
	40–60	2.26 ± 0.02	15.81 ± 4.63	1.63 ± 0.34	1.54 ± 0.13	1.29 ± 0.27	42.27 ± 2.68	9.45 ± 0.32
S3	0–20	2.21 ± 0.03	14.98 ± 0.28	3.00 ± 0.78	11.14 ± 1.10	1.57 ± 0.32	43.73 ± 0.86	10.84 ± 1.27
	20–40	1.91 ± 0.02	14.63 ± 1.85	0.89 ± 0.22	2.72 ± 0.17	1.27 ± 0.43	45.41 ± 6.25	8.35 ± 0.31
	40–60	2.56 ± 0.11	13.52 ± 2.51	3.03 ± 1.19	5.08 ± 0.55	2.01 ± 0.33	51.43 ± 4.08	11.63 ± 0.65
S4	0–20	1.84 ± 0.09	12.8 ± 0.44	2.17 ± 0.26	11.70 ± 0.80	0.56 ± 0.08	21.43 ± 2.70	4.02 ± 0.14
	20–40	2.11 ± 0.25	18.1 ± 0.81	3.60 ± 0.29	3.08 ± 0.19	7.80 ± 3.15	41.30 ± 8.25	8.57 ± 0.88
	40–60	2.32 ± 0.21	9.54 ± 1.72	0.85 ± 0.26	9.70 ± 1.15	1.70 ± 0.50	40.92 ± 3.48	9.35 ± 0.36
S5	0–20	0.60 ± 0.02	39.70 ± 9.29	1.05 ± 0.16	25.92 ± 1.46	1.61 ± 0.59	54.85 ± 1.83	11.12 ± 0.58
	20–40	0.61 ± 0	13.13 ± 3.06	0.26 ± 0.06	6.68 ± 0.98	1.69 ± 0.42	47.89 ± 8.43	11.72 ± 1.55
	40–60	0.56 ± 0.11	19.77 ± 1.86	0.02 ± 0	10.90 ± 1.18	1.75 ± 0.38	51.01 ± 1.99	10.50 ± 1.30
S6	0–20	0.58 ± 0.08	9.17 ± 1.43	0 ± 0	9.90 ± 0.58	0.78 ± 0.13	40.42 ± 6.59	5.84 ± 0.91
	20–40	0.58 ± 0.07	9.56 ± 1.11	0 ± 0	9.09 ± 1.36	0.89 ± 0.34	38.96 ± 1.98	4.16 ± 0.12
	40–60	0.52 ± 0.07	11.19 ± 3.08	0.21 ± 0.03	20.73 ± 2.13	0.84 ± 0.29	38.42 ± 6.04	4.41 ± 0.30

For the flat area, the K values for the HMs were generally higher in samples from S1 (near the river) than samples from S2 and S3 (further from the river). For example, the highest K values for As, Cu, Ni, Pb, and Zn were all in samples from S1. The HM concentrations in the soil samples from near the river were, generally, relatively high because of the influence of river sediment. Zhang et al. [33] found that the mean As, Cd, Cr, Cu, Ni, Pb, and Zn concentrations in sediment from rivers in the Taihu Lake Basin were higher than the background concentrations. For the sloping area, the K values for all of the HMs were higher for samples from S4 and S5 (lower elevation) than for samples from S6 (higher elevation). For example, the lowest mean K values for As, Cd, Cr, Cu, and Ni were all in samples from S6. Leaching by rainwater is one of the most important ways that mobile HMs migrate in soil. Fang [34] simulated HM leaching from soil and found that leaching markedly decreased the concentrations of slightly acid-soluble species, and HMs with relatively active speciation were leached more readily than HMs with less active speciation. Mean annual rainfall in the mountainous study area is > 1600 mm, which is approximately 700 mm more than in flatter areas at the same latitude [35,36]. Gravity will cause HMs dissolved in interflow to migrate down the slope, which will decrease the bioavailable HM concentrations in soil further up the slope.

The K values for the HMs in the vertical soil profiles varied. For the flat area, the highest mean K values for Cd, Cr, Ni, and Zn were observed in soil from 0–20 cm. The mean K values for As, Cu, and Pb were highest in soil from 40–60 cm. For the sloping area, the mean K values for Cd and Zn were highest in soil from 0–20 cm, and the mean K values for Cr and Pb were highest in soil from 40–60 cm. Most HMs in the tea plantation soil from 20–40 cm had relatively low K values, which indicated that the HMs in this soil were not particularly bioavailable. This may have been related to the distribution of the tea plant roots. The tea plant root system is composed of a main root, lateral roots, absorbent roots, and root hairs [37]. The absorbent roots at the ends of the lateral roots are the main tissues that absorb nutrients and water. These roots are generally found at depths of <45 cm and are concentrated at depths of 20–40 cm [21,38]. Non-residual HMs located near absorbent roots will be transported into a tea plant more readily than residual HMs and non-residual HMs not located near absorbent roots. Therefore, non-residual HMs will be found at relatively low concentrations in soil from 20–40 cm in tea plantations and, in particular, old tea plantations.

4.2. Relationships between HM Concentrations in Tea Leaves and Soil

The Pearson correlation coefficient indicates the degree of linear correlation between two variables. Pearson correlation coefficients were used to identify possible associations between HM concentrations in the tea leaves and different fractions extracted from soil. She et al. [39] assessed HM concentrations in tea leaves from six sampling lines in An-tea plantations. The correlation analysis results for the HM concentrations in tea leaves and soil, at different depths, are shown in Table 6.

There were good correlations between the Cd, Cr, Cu, Ni, Pb, and Zn concentrations in tea leaves, F1 fraction of soil, and F2 fraction of soil. This was likely because the HMs in fractions F1 and F2 were mainly present as ions that could easily be absorbed by the tea plant roots and transported to the leaves. The As and Cd concentrations in tea leaves showed good correlations with the concentrations in the F4 fractions and total concentrations in soil but were poorly correlated with the concentrations in the F1 fractions. This was likely because almost all of the As (>97%) was in the residual fraction, which meant that the As concentration in the residual fraction was similar to the total As concentration. Atmospheric deposition is an important source of HMs in tea leaves, which can absorb HMs directly through respiration. The Cu and Zn concentrations in tea leaves correlated well with the concentrations in the F3 fractions. The results, described above, indicate that there are different relationships between the speciation of different HMs in soil and accumulation of HMs in tea leaves.

Table 6. Correlation coefficients for the relationships between heavy metal concentrations in tea leaves and fractions F1–F4 extracted from soil.

Element	Belt	F1			F2			F3			F4			F1 + F2 + F3 + F4		
		20	40	60	20	40	60	20	40	60	20	40	60	20	40	60
Cr	S1	0.998 *	0.999 *	0.250	0.674	−0.671	−0.672	−0.675	−0.675	−0.675	−0.675	0.302	0.302	−0.674	0.264	0.243
	S2	0.149	−0.988	0.247	0.775	−0.931	−0.932	−0.782	−0.931	0.931	0.782	0.782	−0.931	0.782	0.754	−0.931
	S3	0.952	−0.206	−0.731	0.722	0.725	−0.731	−0.727	−0.727	−0.727	0.727	0.727	−0.727	0.728	0.727	−0.728
	S4	−0.848	−0.005	0.012	−0.854	0.861	0.862	−0.012	−0.013	−0.012	0.012	0.012	0.012	0.001	0.036	0.036
	S5	0.753	−0.708	0.957	−0.649	−0.644	−0.651	−0.338	0.338	0.646	−0.646	−0.646	0.646	−0.664	−0.623	0.646
	S6	0.313	0.661	0.648	−0.775	0.779	0.774	0.775	0.775	−0.775	0.159	−0.159	−0.159	0.172	−0.132	−0.18
Cd	S1	0.033	0.032	0.859	0.871	0.867	−0.864	0.864	0.865	−0.866	−0.001	−0.001	0	0.496	0.329	−0.238
	S2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	S3	0.871	0.87	0.866	0.871	−0.865	−0.873	0.004	0.015	0.006	0.866	0.866	0.866	0.822	0.798	0.793
	S4	0.865	0.876	0.881	−0.855	−0.852	−0.864	−0.865	0.858	0.867	0.866	0.866	0.866	0.812	0.917	0.92
	S5	−0.865	0.885	0.858	−0.863	0.866	0.851	0.002	0.862	0.867	0.866	−0.866	0.866	0.702	−0.792	0.899
	S6	−0.854	−0.857	0.86	0.023	−0.019	−0.051	−0.001	−0.005	0.002	−0.866	−0.866	−0.866	−0.835	−0.806	−0.922
Ni	S1	0.958	0.957	−0.956	0.228	0.729	−0.73	−0.957	−0.957	−0.957	−0.957	−0.957	−0.957	−0.958	−0.955	−0.958
	S2	0.697	0.696	−0.697	0.97	−0.969	0.97	0.272	0.272	0.697	0.273	−0.273	0.697	0.29	−0.274	0.705
	S3	0.603	−0.604	−0.602	−0.992	−0.992	0.992	−0.39	−0.39	−0.39	−0.39	0.39	−0.39	−0.387	0.375	−0.386
	S4	−0.695	0.696	0.697	−0.282	−0.274	-	0.274	0.274	−0.274	−0.274	−0.274	0.274	−0.276	−0.261	0.283
	S5	0.41	0.581	−0.539	-	—	-	−0.408	0.995	−0.995	0.995	0.995	−0.995	0.998 *	0.995	−0.995
	S6	-	-	0.271	-	—	-	0.707	0.706	0.707	−0.707	0.707	−0.698	−0.707	0.707	−0.696
Zn	S1	0.991	−0.991	−0.991	−0.379	−0.379	−0.379	0.991	0.991	0.991	−0.379	−0.379	−0.379	−0.279	−0.311	−0.356
	S2	0.807	0.108	−0.108	−0.807	−0.807	0.915	−0.915	−0.915	−0.915	0.807	0.915	0.915	0.739	0.887	0.957
	S3	−0.981	−0.981	−0.981	0.981	0.981	0.981	0.981	0.981	−0.659	0.981	−0.981	−0.981	0.981	−0.981	−0.99
	S4	−0.352	0.352	−0.352	0.352	−0.352	0.352	−0.352	−0.352	−0.352	−0.352	−0.352	−0.352	−0.352	−0.352	−0.352
	S5	−0.767	0.767	0.767	−0.939	−0.939	−0.939	−0.767	0.767	0.767	−0.939	0.767	0.767	−0.994	0.735	0.744
	S6	0.299	−0.299	−0.299	0.677	0.677	0.677	−0.976	−0.976	−0.976	0.677	−0.976	−0.976	0.602	−0.958	−0.955
As	S1	-	-	-	0.861	0.861	−0.86	−0.006	0.01	−0.009	−0.87	−0.87	0.862	−0.868	−0.871	0.86
	S2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	S3	−0.952	-	0.207	0.74	−0.742	0.741	−0.74	0.739	−0.742	0.952	0.952	0.952	0.952	0.952	0.953
	S4	-	0.24	0.255	0.96	−0.96	−0.961	0.961	−0.961	−0.961	−0.24	−0.24	0.24	−0.233	−0.248	0.231
	S5	−0.869	−0.985	−0.861	0.001	−0.866	0.866	0.001	−0.002	−0.001	0	0	0	−0.001	−0.004	0.003
	S6	-	0.512	−0.569	0.403	−0.405	−0.4	−0.408	0.4	0.399	−0.592	−0.592	−0.592	−0.591	−0.592	−0.593
Pb	S1	−0.768	−0.769	−0.938	0.768	−0.939	0.939	0.171	−0.768	0.768	−0.768	0.939	−0.939	−0.216	−0.903	0.981
	S2	0.391	0.392	−0.391	−0.391	0.391	0.391	−0.602	0.602	−0.602	0.391	−0.391	0.391	−0.999 *	0.543	0.062
	S3	0.288	0.288	−0.684	0.289	0.289	0.685	−0.289	0.289	0.289	0.364	0.289	−0.289	0.352	0.289	0.555
	S4	−0.741	−0.741	0.741	−0.741	0.741	−0.741	−0.741	−0.741	−0.741	0.741	−0.741	−0.741	0.741	−0.741	−0.741
	S5	−0.866	−0.866	−0.866	0.866	−0.866	−0.866	0	0	−0.866	0.866	0.866	0	0.675	−0.988	−0.986
	S6	0.978	0.978	0.978	0.309	−0.309	0.309	0.669	0.978	−0.978	−0.309	−0.978	−0.978	0.044	−0.199	−0.997 *
Cu	S1	0.989	0.619	0.637	0.989	0.989	0.622	0.989	0.989	−0.989	−0.989	−0.622	0.622	−0.989	−0.218	0.344
	S2	0.129	−0.128	0.128	0.795	−0.128	−0.128	−0.795	−0.795	0.128	0.128	−0.128	−0.128	0.08	−0.29	−0.128
	S3	−0.475	0.475	−1.000 *	−0.476	−0.475	−0.476	−0.476	−0.476	−0.476	0.476	0.476	1.000 *	0.476	0.476	0.962
	S4	0.917	0.917	0.918	−0.917	−0.917	0.917	0.917	−0.917	0.872	−0.917	0.917	0.917	−0.917	0.917	0.908
	S5	−0.959	−0.959	−0.96	0.959	0.959	−0.959	0.235	−0.959	0.959	0.959	−0.959	0.235	0.9	−0.959	0.252
	S6	0.994	1.000 **	0.985	−0.988	−0.988	−0.988	0.628	0.988	−0.988	0.36	−0.988	−0.988	0.476	−0.987	−0.988

Notes: * and ** indicate significant differences at $p < 0.05$ and $p < 0.01$, respectively.

Markedly different correlation coefficients were found for the relationships between the HM concentrations in tea leaves and soil at different depths. The concentrations of most of the HMs in tea leaves showed good correlations with the sums of the F1 and F2 concentrations in soil from 0–40 cm but were weakly correlated with the sums of the F1 and F2 concentrations in soil from 40–60 cm. This could be attributed to the location of the majority of tea plant roots at a depth of <45 cm. Bioavailable HMs at this depth will be absorbed by the roots and transferred to the leaves, branches, and other organs of the tea plants. Therefore, the HM concentrations in tea leaves will be closely related to the concentrations of bioavailable HMs in the soil at depths of <45 cm.

5. Conclusions

There were considerable differences in the speciation (acid-soluble, reducible, oxidizable, and residual fractions) of the seven HMs in soil samples collected from An-tea plantations in sloping and flat areas. The contributions of Cr, Cu, and Ni in non-residual fractions (acid-soluble, reducible, and oxidizable) to the total concentrations at all soil depths were higher in the samples from the flat area than in the samples from the sloping area. The contributions of Cd and Zn in the non-residual fractions to the total concentrations at all soil depths were higher in the samples from the sloping area than in the samples from the flat area. The contributions of As and Pb in the non-residual fractions to the total concentrations were highest in the topsoil (0–20 cm) from the flat area and 20–60 cm soil layer from the sloping area.

There were large variations between the K values for the HMs in the soil samples from the An-tea plantations; the K values decreased, in the order Pb > Cd > Cu > Zn > Ni > As > Cr. For the samples from the flat area, the K values were generally higher in the S1 samples (collected near the river) than the other samples. For the samples from the sloping area, the K values were higher for the S4 (lowest elevation) and S5 (middle elevation) samples than for the S6 samples (highest elevation). For the samples from the flat area, the mean K values for Cd, Cr, Ni, and Zn were highest in the topsoil (0–20 cm); the mean K values for As, Cu, and Pb were highest in deep soil (40–60 cm). For the sloping area, the mean K values for Cd and Zn were highest in the topsoil (0–20 cm); the mean K values for Cr and Pb were highest in deep soil (40–60 cm). The HM concentrations were generally lower in the 20–40 cm layer than in the other soil layers. This may have been related to the vertical distribution of the tea plant roots within the soil.

The Cd, Cr, Cu, Ni, Pb, and Zn concentrations in fresh tea leaves correlated well with the concentrations in the F1 and F2 fractions of the soil. The As and Cd concentrations in the tea leaves correlated well with the concentrations in the F4 fraction and total concentrations in the soil but were poorly correlated with the concentrations in the F1 fraction. The Cu and Zn concentrations in tea leaves also correlated well with the concentrations in the F3 fraction. Most of the HMs in the with the sums of the concentrations in the F1, and F2 fractions in soil from 0–40 cm tea leaves showed good correlations but were weakly correlated with the sums of the concentrations in the F1 and F2 fractions in soil from 40–60 cm. There were different relationships between the speciation of different HMs in soil and the accumulation of the HMs in tea leaves.

Marked differences were observed between the vertical distributions and bioavailabilities of HMs in soil from the An-tea plantations. Therefore, chemical speciation and vertical distribution data, rather than total concentration data, should be used to evaluate the potential risks posed by HMs. The results presented here improve our understanding of how HM contamination of tea can be prevented and controlled.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr10040664/s1, Figure S1: Cr concentrations found in the different fractions extracted from soil from the An-tea plantation located in a flat area; Figure S2: Cr concentrations found in the different fractions extracted from soil from the An-tea plantation located on a slope; Figure S3: Cd concentrations found in the different fractions extracted from soil from the An-tea plantation located in a flat area; Figure S4: Cd concentrations found in the different fractions extracted from soil from the An-tea plantation located on a slope; Figure S5: Ni concentrations found in the different fractions extracted from soil from the An-tea plantation located in a flat area; Figure S6: Ni concentrations found in the different fractions extracted from soil from the An-tea plantation located on a slope; Figure S7: Zn concentrations found in the different fractions extracted from soil from the An-tea plantation located in a flat area; Figure S8: Zn concentrations found in the different fractions extracted from soil from the An-tea plantation located on a slope; Figure S9: As concentrations found in the different fractions extracted from soil from the An-tea plantation located in a flat area; Figure S10: As concentrations found in the different fractions extracted from soil from the An-tea plantation located on a slope; Figure S11: Pb concentrations found in the different fractions extracted from soil from the An-tea plantation located in a flat area; Figure S12: Pb concentrations found in the different fractions extracted from soil from the An-tea plantation located on a slope; Figure S13: Cu concentrations found in the different fractions extracted from soil from the An-tea plantation located in a flat area; Figure S14: Cu concentrations found in the different fractions extracted from soil from the An-tea plantation located on a slope.

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