

Toxic heavy metal contamination assessment and speciation in sugarcane soil

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Abstract. The increasing heavy metal pollution in the sugarcane soils along the Great Huanjiang River was caused by leakage and spills of Lead (Pb) and Zinc (Zn) tailing dams during a flood event. Copper (Cu), Zn, Pb, Cadmium (Cd), and Arsenic (As) concentrations of soil samples collected from 16 different sites along the Great Huanjiang River coast typical pollution area were analyzed by Inductive Coupled Plasma Mass Spectrometry (ICP-MS). The mean concentrations of Pb, Cd, Zn, Cu, and As in the sugarcane soils were 151.57 mg/kg, 0.33 mg/kg, 155.52 mg/kg, 14.19 mg/kg, and 18.74 mg/kg, respectively. Results from the analysis of heavy metal speciation distribution showed that Cu, Zn, Pb, and Cd existed in weak acid, reducible, and oxidizable fractions, and the sum of these fractions accounted for significant proportions in sugarcane soils. However, the residual fraction of As with high proportion of reducible fraction indicated that this trace element still poses some environmental risk in the sugarcane soils because of its high content. Assessments of pollution levels revealed that the highest environmental risk was aroused by Pb. In addition, moderate to strong Cd and Zn pollution were found, while As has zero to medium level of pollution and Cu has zero level.

1. Introduction

Soil pollution by heavy metals is a significant environmental problem worldwide [1-3]. In particular, heavy metal pollution of surface soils caused by intense industrialization and urbanization has emerged as a serious concern in many developing countries [4-7]. Heavy metal accumulation on the surface soils is affected by many environmental variables, including parent material and soil properties, as well as by human activities, such as industrial production, traffic, farming, and irrigation [8]. The soil is not only a geochemical reservoir for contaminants but also a natural buffer for transportation of chemical materials and elements in the atmosphere, hydrosphere, and biomass. Thus, the soil is the most important component of the biosphere. Irrespective of their sources in the soil, heavy metals can degrade soil quality as well as reduce crop yield and quality of agricultural products, which negatively affects humans, animals, and the ecosystem [9]. Natural and anthropogenic sources are responsible for the heavy metal accumulation in soil [10-12]. The natural source indicates that the trace metal concentration is derived from parent rocks, and the anthropogenic source indicates that the trace metal



concentration originates from mining activities, metal smelting, mineral fertilizer, waste water irrigation, and exhaust emissions [13-14]. In a contaminated farmland, heavy metal pollution often affects a wide of area, but the level of pollution is sufficiently low so that crops could still grow. However, if heavy metals accumulate in the edible parts of the crop to levels that exceed food safety standards, these metals can enter the body and pose risk to human health. A better understanding and evaluation of the distribution and potential hazards of heavy metals in farmland soils are increasingly needed to ensure food safety and public health.

The Great Huanjiang River, which has a total area of over 10,000 (unit), is one of the densest farmland regions in Guangxi province. Before the mid-2000s, the Great Huanjiang River was dominated by farms and rural villages, and the fertile soils were cultivated intensively, growing two to three crops per year. The Great Huanjiang River suffered a catastrophic flood in June 2001, during which the plant, equipment, and tailings of a mineral enterprise upstream of the river were destroyed. Then, a large number of particulate tailings were washed into the river, which resulted in serious heavy metal pollution. This region along the Great Huanjiang River is also featured with the largest sugarcane production in Guangxi province. The heavy metals will accumulate in the sugarcane and then are transferred to human body by consuming sugar once sugarcane soils are contaminated [15]. The total concentration of heavy metals has been used to assess the pollution level of soil by comparing it with background or standard values of heavy metals, and computing a pollution index, such as bioconcentration factor, potential ecological risk index, enrichment factor, and geo-accumulation index (I_{geo}) [16-19]. Heavy metals can lead to harmful effects on animals and humans because of their non-biodegradability, persistency, and potential accumulation [20]. For example, excessive Cd in the body can increase the ratio of renal tubular damage, osteoporosis, and cancer [21]. However, the total heavy metal content can not sufficiently reflect the environment risk assessment of the soil directly, because different fractions of heavy metal play different roles in soils [22]. For example, heavy metals in soils can be fractionated into the following: weak acid fraction (F1), bound to exchangeable and carbonate forms; reducible fraction (F2), bound to Fe/Mn oxides; oxidizable fraction (F3), bound to organic matters; and residual fraction (F4) according to the European Community Bureau of Reference (BCR) sequential extraction procedure [23-24]. Therefore, it is very important to determine the concentration of labile fractions of heavy metals.

Numerous studies have been conducted on the level of heavy metal pollution of agricultural soils, but the distribution, fractions, and environmental risk of heavy metals in sugarcane soils along the Huanjiang River have been sparsely reported. In this work, the heavy metal speciation and contamination assessment of sugarcane surface soils along the Huanjiang River was firstly investigated. The aims of the present study are as follows: (1) to investigate the distribution of heavy metals, namely, Cu, Zn, Pb, Cd, and As, in sugarcane soils located downstream of Huanjiang River; (2) to determine each fraction concentrations of heavy metals in sugarcane soils located downstream of Huanjiang river employing the BCR sequential extraction procedure; and (3) to assess the environmental risk of heavy metal pollution in sugarcane soils located downstream of Huanjiang River with Inductive Coupled Plasma Mass Spectrometry (ICP-MS). Soil contamination was assessed by the I_{geo} and pollution levels index (PLI).

2. Experimental

2.1. Study area & sampling

The Great Huanjiang River is located at northwestern Guangxi, the upstream of which has a large number of non-ferrous metal mines, such as Beishan lead/zinc mine, Yamai steel plant, Duchuan lead/zinc mine, and Xunle lead/zinc mine, etc. In 2001, the Great Huanjiang River suffered a catastrophic flood. The flood washed away the ore dressing enterprises and tailing located upstream of the river, which resulted in the serious heavy metal pollution of approximately 10000 acres of farmlands.

A total of 16 typical sugarcane pollution soil samples were collected in this experiment. The sampling points were concentrated on the sugarcane soils in the 108°18'3" N–108°18'15" N and 24°53'49" E–24°53'50" E grid. The contamination soils were collected only with depth of 0–20.0 cm and approximately 1.0 kg of soil particles were obtained, and then the samples were transported to the laboratory. Before the determination of the total and labile fraction concentration of the heavy metals, the soil samples were air-dried, ground into fine powder with an agate mortar, and sieved through a 100-mesh nylon sieve. The ground samples were stored in polyethylene zip-type bags for further analysis.

2.2. Analytic methods

The heavy metals in the sugarcane soils were analyzed using the national standard methods. The concentrations of Cu, Zn, Pb, Cd, and As in the final solutions were measured by a 7700e ICP-MS (Agilent, USA). The instrument was calibrated prior to each set of measurements, and 50 µg/L of Bi, In, Lu, Rh, and Tb was used as the internal standard. With respect to quality control and assurance, procedural blanks, standard reference materials [certified standard reference estuarine sediment NIST 1646a, and Chinese standard reference soils (GSS1 and GSS8)], and 10% replicates of the sample load were routinely inserted in the digestion sequence. The recovery rates for the target heavy metals in the standard reference materials were reasonably good (90.0 %–105.0%).

The sequential extraction method through the BCR analysis was performed as described by Rauret et al. The BCR method was performed with the following fractions: F1, F2, F3, which were extracted by acetic acid, hydroxylamine hydrochloride, and ammonium acetate solutions, respectively. Soil was sampled from the ground (0 m) to 0.20 m deep for analysis. The method consisted of a three-step sequential extraction procedure which identified three different fractions: i) extraction with 0.11 M acetic acid (pH 2.85), ii) extraction with 0.5 M hydroxylammonium chloride; and iii) digestion with 8.8 M hydrogen peroxide and extraction with 1 M ammonium acetate (pH 2.00). An aliquot of 0.5 g from the solid residue obtained after the third extraction was also digested with aqua regia to yield a residual fraction. Although the authors did not attribute any specific chemical nature to the metals in each fraction, the first step (F1) predominantly released soluble, adsorbed, and exchangeable metals and some carbonates, F2 mainly included metals associated with reducible species (especially some oxides), and F3 included metals in oxidizable forms, especially many organo-metal associations and some sulfides. The residual fraction accounts for the most recalcitrant forms of metals with negligible mobility [25]. The accuracy of the analytical data was assessed through the analysis of the certified reference material BCR-701, that is, sugarcane soils certified for extractable metal contents in the three steps of the modified BCR sequential extraction procedure. The recovery percentage of the sequential extraction was calculated using the following equation:

$$\text{Recovery (\%)} = \frac{F1 + F2 + F3 + F4}{C_{\text{total}}} \times 100\% \quad (1)$$

The recoveries of Cu, Zn, Pb, Cd, and As in each extraction procedure ranged from 89.9% to 100.4%, 99.5% to 109.5%, 88.1% to 101.1%, 100.8% to 112.9% and 88.1% to 101.3%, respectively. The method was proved to be simple and appropriate for application.

SPSS 21.0 and Excel 2007 were used to analyze the relevant data. Principal component analysis (PCA) was employed to infer the hypothetical source of heavy metals (natural or anthropogenic) in soils with the statistical software package SPSS version 21.0. In the PCA, the principal components were calculated based on the correlation matrix, and VARIMAX normalized rotation was used.

2.3. Contamination assessment method of sugarcane soils

The I_{geo} values for the heavy metals were determined using Muller's expression:

$$I_{\text{geo}} = \log_2 \frac{C_n}{1.5(BE_n)} \quad (2)$$

Where C_n is the concentration of heavy metals examined in the sugarcane soil samples, and BE_n is the environmental background concentration of the metal (the soil heavy metal background values of Guangxi was considered. Factor 1.5 is the background matrix correction factor caused by lithospheric effects. The I_{geo} may consist of even grades [26]: 0, unpolluted ($I_{\text{geo}} \leq 0$); 1, unpolluted to moderately polluted ($0 < I_{\text{geo}} < 1$); 2, moderately polluted ($1 < I_{\text{geo}} < 2$); 3, moderately to highly polluted ($2 < I_{\text{geo}} < 3$); 4, highly polluted ($3 < I_{\text{geo}} < 4$); 5, highly to very highly polluted ($4 < I_{\text{geo}} < 5$); and 6, very highly polluted ($5 < I_{\text{geo}} < 10$).

The CF is the ratio obtained by dividing the concentration of each metal in the soil by the baseline or background:

$$CF = \frac{C_{\text{heavy metal}}}{C_{\text{background}}} \quad (3)$$

In this study, soil heavy metal background values of Guangxi were utilized for calculating CF. The contamination levels may be classified based on their intensities ranging from 1 to 6: 0, none ($CF < 1$); 1, none to medium ($1 < CF < 2$); 2, moderate ($2 < CF < 3$); 3, moderately to strong ($3 < CF < 4$); 4, strongly polluted ($4 < CF < 5$); 5, strong to very strong ($5 < CF < 6$); and 6, very strong ($CF > 6$) [26]. To understand the overall level of sugarcane soil pollution across the sampling sites, the PLI was determined as the root of the product of the n CF:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \quad (4)$$

The pollution levels may be defined to four levels based on PLI intensities: no pollution, $PLI < 1$; moderate pollution, $1 < PLI < 2$; heavy pollution, $2 < PLI < 3$; and extremely heavy pollution, $3 < PLI$.

3. Results and discussion

3.1. Spatial distribution and source analysis

The concentrations of heavy metals in the sugarcane soils are shown in Fig.1. The mean concentrations of Cu, Zn, Pb, Cd, and As were 14.19, 155.52, 151.57, 0.33, and 18.74 mg/kg, respectively. In the sugarcane soil samples, the concentrations of Cu, Zn, Pb, Cd, and As were comparable to the soil heavy metal background values of Guangxi. The contents of Zn, Pb, Cd, and As were higher than the background values for Guangxi in all sites, while the content of Cu was lower than the background values for Guangxi in all sites. The results suggest that the Zn, Pb, Cd, and As are severe pollutants in this sugarcane soil. The concentrations of Zn, Pb, Cd and As at all sites (2.5 to 4.4 times, 4.2 to 14.1 times, 2.5 to 7.1 times, 1.1 to 2.6 times, respectively) significantly exceeded the background values for Guangxi, probably because the study sugarcane soils were located downstream of some non-ferrous metal mines, the heavy metals accumulated because of long-term irrigation and the catastrophic flood in 2001. In addition, the mean content of As in the sugarcane soils was also higher than the background values for Guangxi, but was not very significantly (1.1 to 2.6 times) comparable to the contents of Zn, Pb, and Cd. Long-term irrigation in the past, with the pollution water of Huanjiang River, in which the concentration of Cd accumulated in sugarcane soils, may have caused the high Cd content. Moreover, during mining in non-ferrous mines located upper stream, dust and ash containing heavy metals are discharged into the air, so the As may have originated from dry

and wet atmospheric deposition. The As content was not relatively high compared with Zn, Pb, and Cd probably because remediation of heavy metals by adding a passivator and planting hyperaccumulator have achieved some effects. Nevertheless, the concentration of Cu in the sugarcane soils was lower than the background values for Guangxi. This result indicated that remediations of heavy metals using a passivator and planting hyperaccumulator are useful in reducing Cu accumulation in the sugarcane soils. Additionally, the chelation and antagonism between heavy metals may be the other causes, which resulted in the lower Cu concentration than the background values for Guangxi.

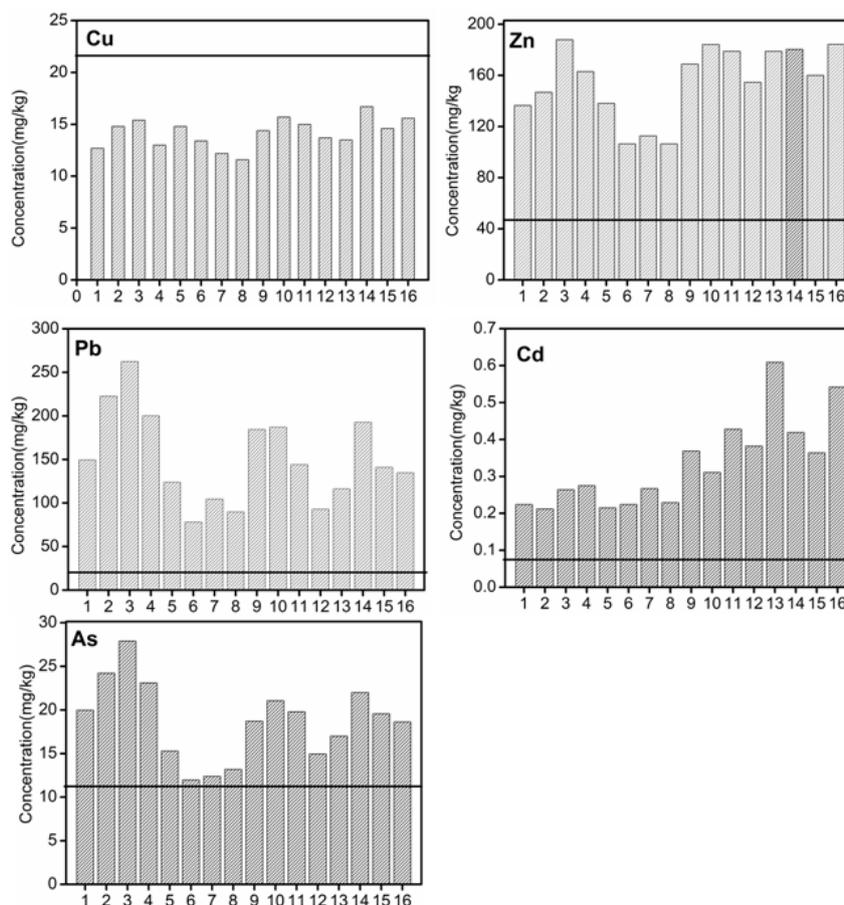


Figure 1. The distribution of heavy metals in the sugarcane soils.

Table 1. The total variance explained and rotated component matrix for heavy metals in the sugarcane soils.

Component	Initial eigenvalue			Rotation sums of squared loadings			Element	Principal Component	
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %		PC1	PC2
1	3.143	62.853	62.853	2.588	51.759	51.759	Pb	0.981	- 0.001
2	1.374	27.484	90.337	1.929	38.578	90.337	As	0.963	0.162
3	0.390	7.796	98.133	-	-	-	Cd	- 0.162	0.951
4	0.050	1.002	99.136	-	-	-	Zn	0.612	0.761
5	0.043	0.864	100.000	-	-	-	Cu	0.545	0.648

To identify the source of heavy metals in the studied sugarcane soils, PCA was performed, because it has been considered as an effective method for the source identification of heavy metals. The PCA results of the heavy metal content are shown in Table 1. The first principal component (PC1) explained the greatest variance (51.8%), which included Pb and As. The second principal component (PC2) included Cd, Zn, and Cu, accounting for 21.7% of the total variance. PC1 could be better explained as a mixed source from both anthropogenic and lithogenic sources specifically derived from non-ferrous mine effluent. Pb usually originated from the waste water of the Pb-Zn mine upstream of the river and the residue of tailings washed away by the flood in 2001. In addition, As was a lithogenic and atmospheric component. The dust and fly ash derived from the upper steam non-ferrous was the main source of As. This result suggested that Pb and As are from the natural and industrial sources.

The PC2 mainly consisted of Cd, Zn, and Cu. High Cd and Zn contents as pollutants of sugarcane soils from tailing washed away by flood and wastewater of mining and planting. However, the content of Cu was lower than the background value for Guangxi. Additionally, Cu also originated from mining, but Cu was effectively decreased by passivator and hyperaccumulator. The mining activities contributed to the Cd, Zn, and Cu contents in sugarcane soil.

3.2. Speciation of heavy metals

A well-known BCR method of sequential extraction procedure was used to assess the relative mobility and distribution of trace elements in soil. Different fractions of heavy metal in the soils have different availabilities to sugarcane. Several differences among the speciation distributions of the different heavy metals, and the available forms of Cu, Zn, Pb, Cd, and As in contaminated sugarcane soil results are shown in Fig.2, Cu and Zn had similar fraction distributions in the 16 sampled soils. The sum of F1, F2, and F3 accounted for significant proportions in Cu and Zn as 59.50% and 53.01%, respectively. The F4 proportions in Cu and Zn element were 40.50% and 46.94%, respectively. This result indicated that Cu and Zn pose persistent threat to the ecosystem and plants. Furthermore, the total concentration of Cu was slightly above the background value for Guangxi, and the environmental risk of Cu may be low in the sugarcane soils. For Pb and Cd element, the sum of F1, F2 and F3 accounted for significant proportions of 91.60% and 8.40%, respectively. The order of various fractions of Pb was F2 (74.90%) > F3 (10.02%) > F4 (8.40%) > F1 (6.68%). The order of various fractions of Cd was F1 (56.41%) > F2 (16.84%) > F3 (16.83%) > F4 (9.92%). The F4 proportions in Pb and Cd were 8.40% and 9.92%, respectively. The residual fraction accounts for the most recalcitrant forms of metals with negligible mobility [25]. The low F4 results of Pb and Cd indicated that the residual fraction of element is likely to be released and with considerable environmental risk. Pb and Cd element have remarkable bioavailabilities and can be easily circulated in the food chain, thus threatening human health and environment. This fact indicated that other effective measures should be undertaken to decrease the pollution.

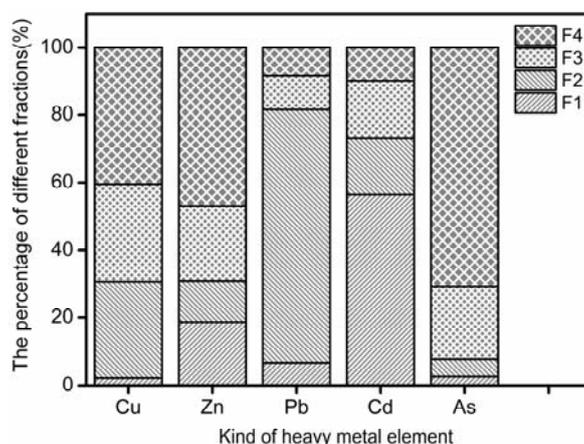


Figure 2. The percentage of heavy metal different fractions in the sugarcane soil.

The order of different fractions of As was F4 (70.70%) > F3 (21.59%) > F2 (5.05%) > F1 (2.66%). The sum of F1, F2, and F3 accounted for a significant proportion in As with mean percentage of 29.30%. The F4 (residual fraction) proportion of As was 70.70%. The high F4 result of As indicated that the residual fraction of As is unlikely to be released and with no environmental risk. Nevertheless, a potential risk still exists because of the high total concentration of As.

3.3. Contamination assessment and environmental risk

Table 2 shows the assessment of the heavy metal pollution and environmental risk of the sugarcane soils using I_{geo} , CF, and PLI. The three assessment methods of heavy metal based on the soil heavy metal background value for Guangxi can show the extent of external pollution. The I_{geo} values for the corresponding elements were as follows: Cu, -1.45 – -0.92; Zn, 0.73 – 1.55; Pb, 1.49 – 3.24; Cd, 0.72 – 2.24; As, -0.45 – 0.77. Overall, the average order of I_{geo} was Pb (2.36) > Cd (1.29) > Zn (1.25) > As (0.16) > Cu (-1.17). The I_{geo} values indicated that the studied metals in the sugarcane soil were from unpolluted to moderately polluted status to highly polluted status. Among the environmentally most heavy metals, Zn, Pb, and Cd showed significant accumulation in the sugarcane soils, as indicated by their corresponding mean I_{geo} values of 1.25 ± 0.28 , 2.36 ± 0.51 , and 1.29 ± 0.48 , which suggest that high concentrations of Zn, Pb, and Cd can transfer from soil to sugarcane. By contrast, the I_{geo} value of Cu (-1.17 ± 0.15) was less than zero, which indicates that the sugarcane soil was not polluted by Cu. Moreover, the I_{geo} value of As (0.16 ± 0.35) was less than one, suggesting that the sugarcane soils were unpolluted to moderately polluted by As, with little environmental risk.

Table 2. The heavy metal pollution and environment risk assessment of the sugarcane soils by I_{geo} , CF and PLI.

Sample	Cu		Zn		Pb		Cd		As		PLI
	I_{geo}	CF	I_{geo}	CF	I_{geo}	CF	I_{geo}	CF	I_{geo}	CF	
1	-1.32	0.60	1.08	3.18	2.43	8.06	0.80	2.61	0.29	1.83	2.36
2	-1.10	0.70	1.19	3.42	3.00	11.99	0.72	2.47	0.57	2.22	2.75
3	-1.04	0.73	1.55	4.38	3.24	14.14	1.04	3.08	0.77	2.56	3.24
4	-1.29	0.62	1.34	3.80	2.85	10.79	1.10	3.21	0.50	2.12	2.80
5	-1.10	0.70	1.10	3.22	2.15	6.66	0.74	2.51	-0.10	1.40	2.21
6	-1.24	0.63	0.73	2.48	1.49	4.22	0.80	2.61	-0.45	1.10	1.80
7	-1.38	0.58	0.81	2.63	1.91	5.63	1.05	3.11	-0.40	1.14	1.98
8	-1.45	0.55	0.73	2.48	1.69	4.84	0.83	2.67	-0.31	1.21	1.84
9	-1.14	0.68	1.39	3.94	2.73	9.94	1.52	4.30	0.19	1.72	2.88
10	-1.01	0.74	1.52	4.29	2.75	10.08	1.27	3.62	0.37	1.93	2.95
11	-1.08	0.71	1.47	4.17	2.37	7.76	1.73	4.99	0.28	1.82	2.91
12	-1.22	0.65	1.26	3.60	1.74	5.00	1.57	4.45	-0.13	1.37	2.35
13	-1.23	0.64	1.47	4.17	2.06	6.26	2.24	7.10	0.06	1.56	2.84
14	-0.92	0.79	1.49	4.20	2.79	10.39	1.70	4.88	0.43	2.02	3.21
15	-1.12	0.69	1.31	3.73	2.34	7.59	1.50	4.24	0.26	1.79	2.72
16	-1.02	0.74	1.52	4.30	2.28	7.26	2.07	6.32	0.19	1.71	3.01

Based on the assessment result of CF, the CF ranges for the corresponding trace elements are as follows: Cu, 0.55 – 0.79; Zn, 2.48 – 4.38; Pb, 4.22 – 14.14; Cd, 2.47 – 7.10; and As, 1.10 – 2.56. The order of mean CF was Pb (8.16) > Cd (3.89) > Zn (3.62) > As (1.72) > Cu (0.67). The CF values indicated that Pb, Cd, and Zn were the primary pollutants, because the mean concentration level of Pb was very strong ($CF > 6$) and the mean concentration levels of Cd and Zn were moderately to strong ($3 < CF < 4$). The order of PLI was 3 (3.24) > 14 (3.21) > 16 (3.01) > 10 (2.95) > 11 (2.91) > 9 (2.88) > 13 (2.84) > 4 (2.80) > 2 (2.75) > 15 (2.72) > 1 (2.36) > 12 (2.35) > 5 (2.21) > 7 (1.98) > 8 (1.85) > 6 (1.80). This result showed that three sampled sites were in moderate pollution ($1 < PLI < 2$), ten in heavy

pollution, and three in extremely heavy pollution. In our study area, mine activities discharge a great number of wastewater containing heavy metals into Huanjiang River, which is the main water source for irrigation. In addition, a larger number of tailing containing heavy metals were washed away by the flood in 2001, which resulted in the heavy pollution to Huanjiang River. Long-term irrigation using polluted water from Huanjiang River should be the primary reason that leads to high contamination level of heavy metal in the sugarcane soil.

4. Conclusion

Pb, Cd, As, and Zn were the major metal pollutants, and their concentrations in all soil samples were higher than the heavy metal background value for Guangxi. Pb originated from the waste water of the Pb-Zn mine upstream of the river and the residue of tailings washed away by the flood. By contrast, As was derived from lithogenic and dust or fly ash of mining. Cu, Cd, and Zn were from the tailing washed away by flood and waste water of mining and planting. Natural and industrial sources contributed to the heavy metal content. Pb, Cd, Zn, and As had high pollution levels, and the sugarcane soils were polluted severely. Pb posed highest environmental risk. Cd and Zn were in moderately to strong pollution status. By contrast, As was considered to pose none to medium level of pollution, with little environmental risk, while Cu is a nonpollutant without environmental risk. Cu, Zn, Pb, and Cd pose persistent threat to the ecosystem and human health. The present study reveals the influence of mining activities and flood destruction on sugarcane soils along the Huanjiang River, a polluted river, and another effective method should be undertaken to improve the contamination status.

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