



Metal and metalloid sources apportionment in soil of two major agroecosystems of southern China

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Abstract Apportioning the sources of metals/metalloids is a critical step toward soil quality protection and ecological restoration. The objective of this study was to identify the potential sources of contamination of As, Cd, Cr, Cu, Hg, Mn, Pb, and Zn, and determine the contribution rates of each source, to rice and sugarcane agroecosystems of southwestern Guangxi, southern China. We collected a total of 300 soil samples at a former lead–zinc mine and at two reference sites, 6 and 60 km away from the mine, sampling both agroecosystems at each site. Overall, the positive matrix factorization (PMF) receptor model revealed that in rice paddies at the mine site, mining activities had the highest contribution (60.7% of all examined

metals/metalloids), followed by irrigation (25.8%), and agrochemical application (13.5%). At the close reference site, agrochemical application contributed 42.8%, followed by irrigation (22.7%), natural sources (17.4%), and mining activities (17.2%). At the far reference site, agrochemical application was predominant (40.6%), followed by irrigation (32.5%), and natural sources (26.9%). In comparison, at the mine site and the close reference site in sugarcane ecosystems, agrochemical application was predominant (50.1% and 57.4%, respectively), followed by mining activities (49.9% and 42.6%). At the far reference site, agrochemical application contributed 51.2%, followed by natural sources (48.8%). Therefore, the PMF model indicated that the optimal solution was four or three sources per site for rice paddies, but only two sources per site for sugarcane, suggesting that sources of

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metal/metalloid contamination were more complicated in rice paddy than in sugarcane agroecosystems.

Keywords Contamination of agricultural soil · Daxin lead–zinc mine tailings · Metals and metalloids · Rice paddy · Source apportionment · Sugarcane

Introduction

Metal and metalloid contamination of agricultural soil has now become an issue of public concern, because it deteriorates soil functioning, degrades soil quality, and eventually makes crops and groundwater unfit for consumption by humans and other organisms (Hou et al., 2014; Lu et al., 2015; Qu et al., 2016). The release of metals and metalloids into farming lands via the application of various agrochemicals is increasing in different regions worldwide, due to the growing global human population and elevated demand for food (Hu et al., 2018; Huang et al., 2015). Along with agrochemical use, other sources, including atmospheric deposition, mining activities, waste disposal, wastewater irrigation to crops, as well as the use of sewage sludge, are also responsible for releasing metals and metalloids in agricultural lands (Hou et al., 2014; Lu et al., 2012).

China has experienced a major problem due to the pollution of arable lands, a problem made complex by the country's highly diverse agricultural ecosystems, soil and geological types (e.g., karst terrains), and high metal and metalloid geological background (Hou & Li, 2017). However, in 2016, China came up with the action plan called "Soil Pollution Prevention and Control Action Plan" to clean up nearly 700,000 ha of severely polluted farmlands by 2020 and efficiently use about 95% of the country's polluted land safely by 2030 (Hou & Li, 2017; Hou et al., 2020; Qu et al., 2016). The target for such an action plan was to demonstrate the efficacy of restoration or remediation projects by 2020 at around 200 majorly polluted sites, convert approximately 1.3 million ha of severely contaminated arable lands into either grasslands or forests, as well as alter the cultivating techniques of nearly 2.7 million ha of moderately contaminated arable lands (Hou & Li, 2017). To achieve such an action plan fully, much capital investment is needed. Indeed, those responsible for the pollution should be subjected to the payment of the expenses, while the Chinese government will also be required to assist in paying clean-up costs of contaminated soils (Qu et al., 2016).

Understanding the total concentrations of metals and metalloids in a particular ecosystem may give fundamental information regarding the degree and magnitude of metal and metalloid pollution. However, this information is not enough for a detailed assessment of the sources of metals into the ecosystem (Komárek et al., 2008). Many studies have been done to distinguish anthropogenic and geological-based sources (hereafter, sources apportionment) of different metals/metalloids in abiotic samples in various countries worldwide. Similarly, when it comes to source apportionment, particularly in agricultural soil in China, there are a substantial number of studies that have been conducted, including Hu et al. (2018), Guan et al. (2019), Han et al. (2022), Liu et al. (2021a), and Wang et al. (2019). These studies have focused on the source apportionment in soil of a single agricultural ecosystem or sometimes in soil of multiple agroecosystems that are receiving similar agronomic treatments (e.g., fertilization and pest management). However, none of these studies has attempted to compare the apportionment of metal/metalloid sources in soil of agronomic crops grown in two different environmental conditions.

Here, we compare source apportionment in two of the most common crops of tropical regions, rice and sugarcane, which have very different methods of agronomy. Rice (*Oryza sativa*) is cultivated in submerged conditions (Ali et al., 2019; Elphick, 2010). The submerged environment deters weeds, as well as safeguarding seedlings from damaging surface temperatures (Elphick, 2010). However, water used to submerge the paddy fields may be contaminated with various metals and metalloids, leading to secondary pollution of paddy soil. Rice is one of the world's staple foods and is particularly dominant in Asia (Mu et al., 2019). In China, for instance, rice is consumed by at least 65% of the citizens in the country (Huang et al., 2013b; Lou et al., 2013). Because of its usage, rice has been shown to be a major source of metal/metalloid exposure. For example, in inland China, rice is the primary exposure route for humans of Hg, instead of the more familiar exposure source of fish (Zhang et al., 2010). In addition, rice is also reported to be the predominant exposure pathway for humans to residues of Cd in China (Lu et al., 2021; Song et al., 2017). A second major economically important crop of southern China is sugarcane (*Saccharum officinarum*). Sugarcane is cultivated in dry environments where there is little or no irrigation (Li & Yang, 2015) and thus is an interesting comparison to rice as to the apportionment of metal/metalloid sources.

We explored the residues of eight metals/metalloids, specifically arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), lead (Pb), and zinc (Zn) from an area that used to be a lead–zinc mining site and a close (6 km distance) and far reference site (60 km distance) in southern China. We collected soil samples both in rice paddy (irrigated by local water sources) and in sugarcane fields (not irrigated) at each of the three sites, which are not connected by any above-ground water source. In a separate study that focuses on metal/metalloid concentrations in both soil and living organisms (Mtemi et al. in review at *Ecotoxicology and Environmental Safety*), we have shown, using these same soil measurements, that Hg, Pb, and Zn had higher soil contamination at the mine site than both reference sites in both agroecosystems, and As and Cd were also similarly elevated in one agroecosystem (Fig. S1). However, the concentrations at all sites were generally within the same order of magnitude, and for some metals/metalloids, concentrations were higher at the reference sites (for Cu in both agroecosystems and for As and Cr in one agroecosystem). Here, our underlying research goals were to (1) identify the possible sources of metal/metalloid contamination at our site and (2) determine how much each potential source contributes, and how these patterns vary among metals/metalloids. We hypothesized that.

1. Other than the known inactive mining source, agrochemicals application, and irrigation water would be additional sources of metal/metalloid contamination in agricultural fields.
2. Mining activities would be associated with cadmium (Cd), lead (Pb), and zinc (Zn) release, because the study site includes Pb/Zn mine tailings.
3. Agrochemical application would be associated with the deposition of copper (Cu) and zinc (Zn) because these metals are among the active ingredients in some agrochemicals. In addition, Cu and Zn are often used in animal feeds as nutritional additives (Liu et al., 2020; Luo et al., 2009; Nagajyoti et al., 2010; Peng et al., 2019; Zhou et al., 2015).

Methodology

Studied sites

This research was conducted in Chongzuo Prefecture, southwestern Guangxi Zhuang Autonomous Region,

southern China (Fig. 1). This area has a subtropical monsoon climate, characterized by a mean temperature of about 25.4 °C and an annual precipitation of about 1000 to 1600 mm (Huang et al., 2013a; Yang et al., 2021). Guangxi is the leading sugarcane producer in China, supplying nearly one-third of the crop harvested in China (Li & Yang, 2015; Xiaofei et al., 2017; Yin et al., 2019). Guangxi Province is also among the provinces in China with the most limestone karst areas (Jiang, 2004; Li, 1996; Yang et al., 2021). Some important features of karst areas are that their soil is enriched with various metals and metalloids (Yang et al., 2021; Zhao et al., 2015). For instance, in Guangxi Province, the natural background of As, Cd, Cr, Cu, Hg, Mn, Pb, as well as Zn residues is higher than Chinese benchmark values of contamination (He et al., 2020; Hu et al., 2020; Yin et al., 2019). Additionally, the region has abundant deposits of various nonferrous metal resources including Zn, as well as Pb (Xiaofei et al., 2017; Yin et al., 2019). Contamination associated with mining activities is an acute problem for the agricultural sector in Guangxi, because of the regional insufficiency of arable lands (Li et al., 2007).

In this study, we chose the Daxin Pb/Zn mine tailings to be the site of sample collection. Mining activities at this site occurred primarily from 1954 to 1995 (Xiaofei et al., 2017). Extraction of metals was stopped in 2001, and the site was completely shut down in 2005 because of pollution of land resources as well as due to the reduced productivity of the mines themselves (He et al., 2020; Xiaofei et al., 2017). The area is currently dominated by agricultural activities; rice, sugarcane, as well as different types of vegetables are the most grown crops in this area (Huang et al., 2013a). The presence of mine tailings in this site has been reported to pollute neighboring agricultural fields (Pan et al., 2020), affect biodiversity (He et al., 2020; Liu et al., 2022; Liu et al., 2021b), and even in some instances, affect the health of humans inhabiting this region (Lv, 2014); hence, the area has been the focus of public attention.

Samples collection

Soil samples were sampled in both agroecosystems at each of the three sites (Fig. 1). In Daxin County, samples were collected from three locations within 12.9 km² of the Daxin Pb/Zn mining district, two of which (Dongling and Shangyu villages) had rice paddy fields,

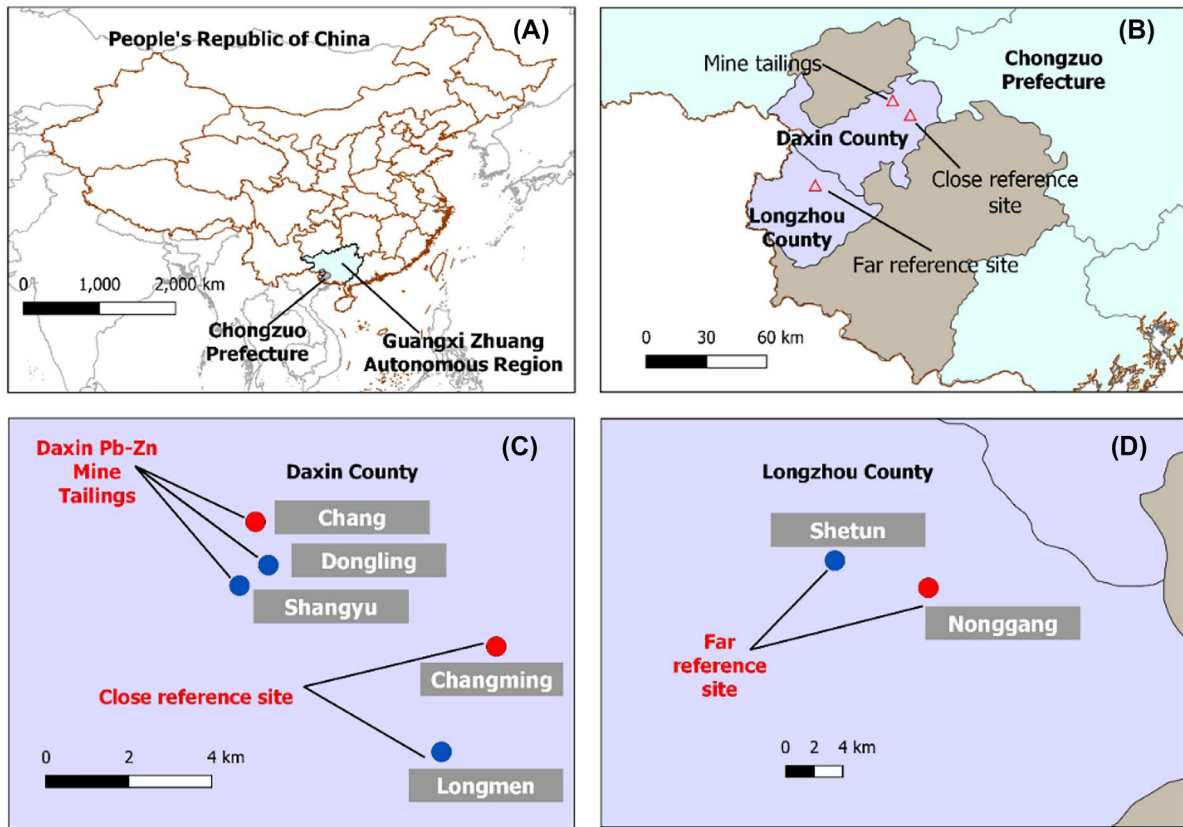


Fig. 1 A map showing the study site as well as sampling locations. Blue locations were rice paddy ecosystems, while red ones were sugarcane ecosystems

and one of which (Chang village) had sugarcane fields. After finding no differences between Dongling and Shangyu villages, we combined these two sites in the analysis. The close reference site was 6 km away from the Daxin Pb/Zn mine tailings, without any above-ground water connection, and was comprised of two sampling locations (Longmen village, which had rice paddy fields, and Changming village, which had sugarcane fields). The far reference site was situated near the Nonggang National Nature Reserve in Longzhou County, nearly 60 km away from the Daxin Pb/Zn mine tailings, and consisted of two sampling locations (Shetun village, which had rice paddy fields, and Nonggang village, which had sugarcane fields; see Fig. 1).

Sampling of soil samples

Soil sampling was done in 50 quadrats, each sized 1 m × 1 m and arranged at least 10 m away from one another,

placed in a 500 m × 500 m sampling area inside the agricultural field. In each quadrat, 12 soil subsamples of nearly 50 g each were collected using an auger at a depth of 0–20 cm and then put together to make a composite sample. The composite soil sample was spread over a clean nylon sheet, and undesirable materials such as stones and roots were removed. Then, about 500 g of the composite sample was collected and put into clean polyethylene sampling bags, and labeled, as well as stored before further procedures in the laboratory (Davidson, 2013).

Samples preparation

All the equipment, glassware, as well as plastic tubes were soaked in 5% HNO₃ solution overnight in the lab, rinsed in the ultrapure water three times, and then oven-dried at 60 °C for around 8 h prior to use (Komarnicki, 2000). Then, all soil samples were air-dried in the laboratory for

nearly 2 weeks and ground afterwards using a well-cleaned agate mortar and pestle into fine soil particles, to attain the homogeneity of soil particles (Davidson, 2013). Finally, the soil particles were passed through a 2 mm sieve made of stainless steel, labeled, and stored in polyethylene bags prior to the metals and metalloids measurement.

Measurement of metals/metalloids residues in soil samples

Total mercury (THg) residues in soil samples were determined through thermal decomposition, amalgamation, as well as atomic absorption spectrophotometry at 254 nm, using the Direct Mercury Analyzer (DMA-80, Milestone Srl) at Guangxi University.

For other metals/metalloids, 65% HNO₃ (guarantee reagent (GR)) was used to digest soil samples via the graphite furnace digestion method in the graphite digestion furnace (PROD60, Zerom, China), by adhering to the guidelines given by Zhao et al. (2018). Briefly, we weighed from 0.22 to 0.56 g of dried and ground soil samples using an analytical balance (HZK-JA510, HuaZhi, China) and put the samples in Teflon decoction tubes. We added 6 ml HNO₃, shook the contents, and covered the tubes using small bent neck funnels. The contents were put on a graphite boiler and heated to ~140 °C for at least 75 min. Then, the contents were cooled down for some minutes, followed by the addition of 6 ml HCl and 2 ml HNO₃, respectively. We shook the contents and placed them back on the graphite boiler and heated up to about 150 °C for at least 50 min. We cooled down the contents for some minutes, then added 6 ml HF, shook the contents, and heated up again at 150 °C for at least 50 min. Thereafter, the contents were allowed to cool down, followed by the addition of 0.5 ml HCl, 1.5 ml HNO₃, and 3 ml HClO₄, respectively. We shook the contents and heated them up on the graphite boiler at 170 °C for at least 120 min to complete the digestion process. Then, we removed the small bent neck funnels from the Teflon decoction tubes, but the contents were still maintained at 170 °C on the graphite boiler to remove excess acids from the contents. The acid-removing process ended when there were at least 2 ml or even less than 2 ml of liquid solutions in the tubes. We cooled down the liquid solutions and rinsed the Teflon tubes using distilled water, followed by the transfer of the liquid solutions into 50 ml vials. Then, we filtered the liquid solutions using 0.45-μm pinhole filter membranes into 15-ml centrifuge tubes. We shook the solutions and kept them in the refrigerator at 4

°C prior to the measurement of metals/metalloids. Then, the residues of As, Cd, Cr, Pb, Cu, Mn, as well as Zn were analyzed using the inductively coupled plasma optical emission spectrometry (ICP-OES; model ICP-5000, Focused Photonics Inc—FPI, China) at Guangxi University. All the results in this study are presented in mg/kg dry weight of metal/metalloid residues.

Measurement of pH in soil samples

Soil pH was determined using a pH meter (PHS-25, Shanghai, China) in a mixture of 5 g soil: 25 ml ultrapure water.

Quality control

For THg, the residues of soil samples were regarded valid if the obtained values were within the given limit of 0.534 to 0.612 mg/kg, which is the 95% confidence interval (CI) of the certified human hair reference material (IAEA-086) (Bleise et al., 2000). The average recovery rate of the certified human hair reference material (IAEA-086) for THg was 100.7±3.8%. The detection limit (DL) of the DMA-80 is 0.2 μg/kg Hg.

For other metals/metalloids, the certified reference soil (GBW07404a (GSS-4a)) and spiked standard solutions were measured after every fifteen samples for accuracy and precision verification. The overall mean recovery rates for the certified reference soil material (GBW07404a (GSS-4a)) were as follows: As: 93.5±6.7%, Cd: 91.3±4.9%, Cr: 102.4±5.2%, Cu: 83.1±4.6%, Mn: 99.6±1.9%, Pb: 102.0±10.7%, and Zn: 103.8±6.1%. Matrix spikes recovery rates of the metals/metalloids were as follows: As: 116.5±3.7%, Cd: 104.7±1.7%, Cr: 96.6±1.4%, Cu: 99.0±1.6%, Pb: 117.8±0.2%, Mn: 99.7±1.5%, and Zn: 87.4±6.7%. We prepared sample blanks in the same way as soil samples to determine the method detection limits. The method detection limits for the ICP-OES in (mg/kg) of the analyzed elements were as follows: As: 0.01, Cd: 0.009, Cr: 0.014, Cu: 0.13, Pb: 0.015, Mn: 0.04, and Zn: 0.4. The limits of quantification in (mg/kg) were as follows: As: 0.03, Cd: 0.027, Cr: 0.042, Pb: 0.045, Cu: 0.394, Zn: 1.21, and Mn: 0.121.

Data analysis

We used the contamination factor (*CF*), degree of contamination (C_{degree}), and modified degree of contamination (mC_{degree}) to assess the pollution status of rice paddy

and sugarcane soil at the mine site and the two reference sites (Chakraborty et al., 2021; Hu et al., 2019). Contamination factor (CF) is employed to investigate the contribution level of each metal/metalloid to pollution status at a specific site (Cabrera et al., 1999; Chakraborty et al., 2021; Hu et al., 2019), and it is quantified as shown in Eq. 1 below.

$$CF = \frac{C_{\text{metal and metalloid}}(\text{sample})}{C_{\text{metal and metalloid}}(\text{background})} \quad (1)$$

where $C_{\text{metal and metalloid}}(\text{sample})$ represents the concentration of each metal and metalloid in soil sample, and $C_{\text{metal and metalloid}}(\text{background})$ stands for the soil regional background or benchmark value of the associated metal and metalloid; we used the Guangxi Zhuang Autonomous Region soil background/benchmark values of the studied metals/metalloids (see Table 1) reported by CNEMC (1990) and Liu et al. (2016) to calculate the CF values. CF is generally classified into four classes based on its value: as low when $CF < 1$, moderate when CF is 1 to 3, considerable when CF is 3 to 6, and very high when $CF > 6$ (Cabrera et al., 1999; Chakraborty et al., 2021; Hu et al., 2019).

Degree of contamination (C_{degree}) tells about the overall pollution status of a specific site and is quantified as the summation of all calculated CF values of all metals/metalloids studied at the site in question (see Eq. 2).

$$C_{\text{degree}} = \sum_{i=1}^{n=8} CF \quad (2)$$

where n indicates the number of metal and metalloids analyzed in soil samples at the specific study site and is summed over the eight metals/metalloids we used in the study. C_{degree} is classified based on the number (n) of metals/metalloids studied: as low when $C_{\text{degree}} < n$, moderate when C_{degree} is n to $2n$, considerable when C_{degree} is $2n$ to $4n$, and very high when $C_{\text{degree}} > 4n$ (Chakraborty et al., 2021).

Modified degree of contamination (mC_{degree}) illustrates the average degree of contamination at a specific site (Abraham & Parker, 2008; Chakraborty et al., 2021; Hu et al., 2019), which is quantified as shown in Eq. 3 below.

$$mC_{\text{degree}} = \frac{C_{\text{degree}}}{n} \quad (3)$$

where C_{degree} shows the degree of contamination and n indicates the number of metal and metalloid analyzed in

soil samples at every study site. The mC_{degree} is classified into seven classes: as very low when $mC_{\text{degree}} < 1.5$, low when mC_{degree} is 1.5 to 2, moderate when mC_{degree} is 2 to 4, high when mC_{degree} is 4 to 8, very high when mC_{degree} is 8 to 16, extreme when mC_{degree} is 16 to 32, and ultrahigh when $mC_{\text{degree}} > 32$ (Abraham & Parker, 2008; Chakraborty et al., 2021; Hu et al., 2019).

In China, there are three classes of the benchmark or baseline values of the Chinese environmental quality standard for soil set by the Ministry of Environmental Protection (MEP) and the Ministry of Land and Resources (MLR) in 1995 (Zhao et al., 2015; MEP/MLR, 2014). Class I benchmark values were set to represent the soil geological background that will be used to protect the regional natural ecosystems against contamination. Class II values depend on soil pH and were set to safeguard agricultural production, as well as human safety through food chain. Class III values were set to buffer crops and/or forests against phytotoxicity (Zhao et al., 2015; MEP/MLR, 2014). The report demonstrates that we should consider whether the soil is contaminated with a particular metal and metalloid only if its residues exceed the given class II values; the degree of contamination is categorized as light, medium, and severe when the residues are 1 to 3, 3 to 5, and > 5 times class II baseline value, correspondingly.

For source apportionment of metals/metalloids, data were analyzed using receptor models. Receptor models are mathematical models used for calculating or computing sources' contributions to samples based on the compositions or signatures of the contributing sources (USEPA, 2014). A speciated data set is expressed as a data matrix X of i by j dimensions, where i stands for the number of samples and j represents the chemical species that were quantified in the sample (i.e., metals/metalloids), with uncertainty u . The overall objective of receptor models is to calculate the chemical mass balance (CMB) between the determined chemical species concentrations in the sample and source profiles, as illustrated in Eq. 4, with the number of factors p , the species profile f of each source, as well as the amount of mass g each factor contributes to every individual sample (Alleman et al., 2010; Brown et al., 2015; USEPA, 2014).

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (4)$$

where e_{ij} represents the residual for every chemical species or sample.

Table 1 The level of contamination of rice paddy and sugarcane soil at the mine site and two reference sites of southwest Guangxi, southern China, using various pollution indexes, including contamination factor (*CF*), degree of contamination (C_{degree}), and modified degree of contamination (mC_{degree}). The presented index values are based on mean and standard deviations in 50 soil samples at each site in each agroecosystem

		Sites											
		Mine			Close reference			Far reference					
Agroecosystem	Metal and metalloid	Guangxi background (CNEMC, 1990; Liu et al., 2016)	<i>CF</i>	C_{degree}	mC_{degree}	<i>CF</i>	C_{degree}	mC_{degree}	<i>CF</i>	C_{degree}	mC_{degree}		
Rice paddy	THg	0.15	2.4±0.6	447.0±378.6	55.9±47.3	1.6±0.2	234.3±411.2	29.3±51.4	1.4±0.1	226.9±252.2	28.4±31.5		
	As	20.5	1.1±1.1			3.2±2.4			2.3±1.6				
	Cd	0.267	222.7±183.5			166.6±352.5			158.4±196.6				
	Cr	82.1	1.2±1.0			3.2±5.2			6.5±15.1				
	Pb	24	15±13.6			7.8±6.2			6.2±3.9				
	Cu	27.8	4.9±4.4			13.9±9.3			10.1±6.2				
	Zn	75.6	193.4±168.7			31.3±25.8			35.2±24.5				
	Mn	446	6.3±5.7			6.7±9.6			6.8±4.2				
	THg	0.15	1.8±0.1	156.7±38.1	19.6±4.7	1.6±0.1	91.6±17.9	11.5±2.2	0.9±0.1	118.4±17.6	14.8±2.2		
	As	20.5	2.8±0.7			1.8±0.4			0.5±0.3				
Sugarcane	Cd	0.267	81.3±20.7			45.3±7.9			81.7±10.3				
	Cr	82.1	1.5±0.3			3.2±4.8			4.3±1.6				
	Pb	24	10.7±3.3			3.9±0.5			3.5±0.3				
	Cu	27.8	3.1±1.1			6.7±1.0			5.0±2.7				
	Zn	75.6	44.6±9.3			18.5±1.7			14.1±1.1				
	Mn	446	10.9±2.6			10.6±1.5			8.4±1.2				

The CMB equation can be calculated through various models. One such model is the EPA positive matrix factorization (PMF); EPA PMF version 5.0 was used in this study. PMF partitions a speciated sample data matrix into two matrices, including the factor contributions (G), as well as factor profiles (F) to comprehend the potential sources or factors affecting the speciated sample data (Brown et al., 2015; Paatero et al., 2014). The factor profiles (F) are specified to describe the contributing source factors to the sample through the determined source profile details (USEPA, 2014). The observed outputs are constrained to be positive so that no sample could have considerable negative source contributions (Brown et al., 2015; USEPA, 2014).

The PMF receptor model minimizing the object function Q shown in Eq. 5 determines factor contributions (G), as well as factor profiles (F) (Paatero, 1997; Wang et al., 2009).

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik}f_{kj}}{u_{ij}} \right]^2 \quad (5)$$

where Q represents the summation of the squares of the variation (i.e., e_{ij}) between the measured metal/metalloid concentrations (x_{ij}) and the PMF result ($g_{ik}f_{kj}$), weighted by the uncertainties (u_{ij}) of the measured chemical species in the samples.

Q is a fundamental tool for PMF, and during the model operations, two versions of Q , Q (true) and Q (robust), are shown (USEPA, 2014). Q (true) represents the goodness of fit factor quantified comprising all the data points. In contrast, Q (robust) stands for the goodness of fit factor quantified disregarding data points not well fit by the model, which are referred to as samples having residuals larger than four (USEPA, 2014).

Estimation of uncertainties

The use of PMF relies on the calculated uncertainties for each of the chemical species/elements and data points (Kim & Hopke, 2004; Liu et al., 2005; USEPA, 2014). The calculated uncertainties are fundamental tools in the PMF model because they lower the weight of missing values, as well as the below detection limit values in the model (Kim & Hopke, 2004). In this study, we used the procedures by Polissar et al. (1998),

USEPA (2014), and Kim and Hopke (2004) to give each measured data point its corresponding uncertainty as presented in Eqs. 6 and 7 below; all the measured concentrations and their assigned uncertainties were the input files in the PMF model. In this study, almost all scaled residuals of analyzed metals and metalloids were in the range of +3 to -3.

When the concentration (x_{ij}) is \leq MDL (method detection limit), the uncertainty (u_{ij}) is quantified as follows:

$$u_{ij} = \frac{5}{6} \times MDL \quad (6)$$

When the concentration (x_{ij}) is $>$ MDL, the uncertainty (u_{ij}) is quantified as follows:

$$u_{ij} = \sqrt{(\sigma \times x_{ij})^2 + (0.5 + MDL)^2} \quad (7)$$

where σ represents the relative standard deviation of each metal/metalloid in each measured sample.

Treatment of data values

We used box plots to check for extreme values (herein, outliers) of each chemical species or element. Outliers can be deleted, with the disadvantage that this procedure can bias the results to only detect high contamination (Alleman et al., 2010). In addition, outliers can be substituted by either mean or median values of the chemical species/element in question, with uncertainties of four times the means (Alleman et al., 2010; Brown et al., 2015; Juntto & Paatero, 1994; Kim & Hopke, 2004; USEPA, 2014). In our case, outliers were replaced with the mean of a particular chemical species/element in this way. The number of outliers of each metal and metalloid that were replaced by the means is shown in Table S1.

Chemical species/elements categorization

PMF deploys both sample concentrations, as well as user-specified uncertainties related to the sample data set to weight individual points (USEPA, 2014). Therefore, input data files for the PMF models were the concentrations of the eight chemical species (As, Cd, Cr, Cu, Mn, Pb, THg, and Zn) and their associated uncertainties in soil samples at each study site in each agroecosystem. Upon loading the input files in the PMF model, all elements/

chemical species were classified as either strong, weak, or bad based on their concentration/uncertainty ratios, also known as signal/noise ratios (S/N) (USEPA, 2014). In this study, all eight chemical species were deemed strong at the mine site and close reference site in rice paddy agroecosystems. Total mercury (THg) was deemed “weak” at the far reference site in rice paddy agroecosystems and at all three sites in sugarcane ecosystems. Similarly, As was deemed “weak” at both close and far reference sites in sugarcane agroecosystems.

Selection of source factors

To choose the number of source factors, it is fundamental to examine various sources and examine how results change with different numbers of source categories (Kim & Hopke, 2004). We ran PMF models with two to five source factors and examined how the outputs changed. PMF models were initially run 20 times with each source factor. Random seeds were used in each run in the model to find the minimum Q . Based on the minimization of Q values and the residuals, displacement analysis (DISP), bootstraps (BS) mapping, and bootstrap-displacement analysis (BS-DISP) results, models with two factors were seen to be suitable at all three sites in sugarcane ecosystems. In contrast, at the mine and far reference sites in rice paddy agroecosystems, models with three factors were deemed optimal. In addition, at the close reference site in rice paddy agricultural ecosystems, a model with four source factors was deemed optimal.

Error estimation (EE) results

No error code was observed in the DISP, inferring that the obtained results are considered valid (USEPA, 2014). The decrease in Q for both DISP and BS-DISP was within the accepted range (i.e., less than 1% Brown et al., 2015; USEPA, 2014)). In addition, we observed no swaps in all factors for the DISP, and only a few swaps in BS-DISP runs, with over 94% successful BS-DISP runs (Tables S2–S7), inferring that our models or solutions had no or few errors and were well defined (Brown et al., 2015). In this study, all the selected optimal factors had BS of more than 80%, signifying that all the source factors were well reproduced or mapped during BS resampling, and uncertainties used were suitable.

Results and discussion

The main objective of this study was to identify the potential sources of metal/metalloid contamination and the contribution rate of each source, comparing between rice and sugarcane agroecosystems of southwestern Guangxi, southern China. However, before presenting and discussing the source apportionment results, we would like to emphasize first the levels of metal/metalloid contamination in soil and how they differed between the mine and reference sites and between the agroecosystems.

Contamination factor (CF), degree of contamination (C_{degree}), and modified degree of contamination (mC_{degree}) results

The results indicated that Cd, Zn, and Mn had very high contamination factors (the highest category of contamination, CF value > 6 each) at all three sites in both agroecosystems (Table 1). Lead (Pb) had very high CF at all three sites in rice paddy agroecosystems; in sugarcane ecosystems, Pb also had very high CF at the mine site and considerable CF ($CF=3$ to 6) at both reference sites. Copper also had either very high or considerable CF at all sites. Other metals/metalloids showed lower contamination. Chromium had one very high, three considerable, and two moderate measurements. Arsenic had one considerable, four moderate, and one low measurement. Total Hg had all moderate measurements, except for a low reading at the far reference site in sugarcane ecosystems.

Considering all metals/metalloids, both agroecosystems at all three sites had a very high degree of contamination ($C_{degree} > 4n$, i.e., > 32 , where n (number of metals/metalloids) = 8 in this study; Table 1). Similarly, the average modified degree of contamination (mC_{degree}) was ultrahigh at the mine site ($mC_{degree} > 32$) and extreme at both reference sites ($mC_{degree} = 16$ to 32) in rice paddy ecosystems. In sugarcane ecosystems, the average mC_{degree} was extreme at the mine site ($mC_{degree} = 16$ to 32) and very high at both reference sites ($mC_{degree} = 8$ to 16). These results indicate that metals and metalloids show heavy pollution at all three sites (mine site, close reference site, and far reference site) in both rice paddy and sugarcane ecosystems. This pollution status was mostly contributed by Cd, which had a very high contamination factor (CF), followed by Zn, Mn, Pb, and Cu. Contamination factors (CF s) of Pb and Zn were highest at the mine site, as would be

expected for a lead/zinc mine. Cadmium was also high at the mine site because it is usually associated with Pb/Zn metals. As to the other metals, we argue elsewhere (Mtemi et al., in review) that it is likely they are derived from contamination due to irrigation or agrochemicals, although from the levels of metals/metalloids in soil alone, it was previously not clear what source contributes most.

Source apportionment in agricultural soil

Metal and metalloid sources apportionment as estimated by the PMF model in agricultural soil samples at different sites in rice paddy and sugarcane ecosystems are shown in Table 2 (concentrations) and Fig. 2 (percentage contribution).

The first source factor in Table 2 and Fig. 2 likely indicates agrochemical application. This source factor was dominated by Zn residues at all three sites in both rice paddy and sugarcane ecosystems. Other dominant metals in this source factor were Cu, Mn, and Pb that were observed at both reference sites in rice paddy and sugarcane agroecosystems; Cu, Mn, and Pb were also noticeable in this factor at the mine site in sugarcane ecosystem. Chromium and THg contributed at the mine site and in one of the reference sites, both in rice paddy and sugarcane agricultural ecosystems. Cadmium was observed at the far reference site in both rice paddy and sugarcane ecosystems; Cd residues were also seen at the mine site and the close reference site in sugarcane ecosystems. In addition, in this factor, As concentrations were more noticeable in sugarcane ecosystems than in rice paddy ecosystems at all three sites.

Long-term application of synthetic/inorganic fertilizers, especially those originating from phosphate rocks, e.g., diammonium phosphate (DAP), NPK compound fertilizers, monoammonium phosphate (MAP), and superphosphate (SSP), may lead to the elevated concentrations of As, Cd, Cr, Cu, Pb, Mn, THg, Zn and other elements in agricultural ecosystems (Luo et al., 2009; Peng et al., 2019; Zhao et al., 2015). Physiological metals such as Cu, Zn, Mn, and Cr are among the metals that are often used in animal feeds as additives for nutritional purposes, diseases control, and the general well-being of animals (Liu et al., 2020; Luo et al., 2009; Nagajyoti et al., 2010; Peng et al., 2019; Zhou et al., 2015). Despite As being banned for use as additives in animal feeds in Europe, in some

countries such as China and the USA, it is still in use (Li & Chen, 2005). Hence, the use of organic fertilizers and specifically livestock and poultry manure in agricultural production could lead to contamination of land resources with these metals/metalloids (Liu et al., 2020; Luo et al., 2009; Nagajyoti et al., 2010; Peng et al., 2019; Zhou et al., 2015). Pesticide use in controlling diseases, weeds, and insect pests could also be a source of metal contamination, especially Cu and Zn in agricultural farms. Indeed, Cu is a major, and Zn a minor, component of most fungicides, e.g., Mancozeb and CuSO_4 (Belon et al., 2012; Li et al., 2020; Liu et al., 2021a; Luo et al., 2009). We observed at our study sites that various agrochemicals such as pesticides and fertilizers (both organic and synthetics) are extensively applied to the rice paddy and sugarcane crops to promote growth, as well as to control diseases and various weeds and insect pests.

The second source factor likely represents mining activities. In this source factor, Cd, Cu, Mn, and Zn were the dominant metals at both the mine site and the close reference site in rice paddy and sugarcane ecosystems. Other important metals in this factor were Pb and Cr, which were noticeable at the mine site both in rice paddy and sugarcane ecosystems; Pb residues were also seen in this factor at the close reference site in sugarcane agroecosystem. Total mercury concentrations were found at the close reference site in both rice paddy and sugarcane agroecosystems; THg was also observed at the mine site in the sugarcane ecosystem. Furthermore, in this source factor, As residues were found at the mine site and the close reference site in sugarcane agricultural ecosystems.

Pollution of agricultural lands, particularly in rice paddy and sugarcane fields, by Cd has been occurring in China largely in areas associated with mining as well as the smelting of nonferrous metallic ores of lead, zinc, and copper (Hu et al., 2016). Cadmium is a toxic by-product metal associated with Pb–Zn mines (Alloway, 2013; Mishra et al., 2019; Nagajyoti et al., 2010), and PbS and ZnS are major compounds found in Pb–Zn mines (Alloway, 2013; Liu et al., 2013; Mishra et al., 2019). Furthermore, residues of Cr and Mn (Du et al., 2019; Huang et al., 2020; Shu et al., 2003) as well as As and Cu (Alloway, 2013) can also be found in Pb–Zn mining regions. In addition, Zn ores have been demonstrated to be associated with extraordinary Hg concentrations (Alloway, 2013). All these associations between metal/metalloids and

Table 2 Source factor contributions for various metals/metalloids in agricultural soil samples as estimated by the PMF model. “-” means the absence of a particular source factor at the study location in question. Bolded values in each source factor indicate

metals/metalloids that were above the class II baseline values of the Chinese environmental quality standard for soil, shown in the supplemental table (Table S8). Baseline values of manganese (Mn) were not stipulated in the report of MEP and MLR

Sites	Species	Concentrations (mg/kg) for each source factor				Concentrations (mg/kg) for each source factor			
		Rice paddy agricultural ecosystem				Sugarcane agricultural ecosystem			
		Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 4
Mine	As	0.0000	0.0000	22.57	-	26.82	33.25	-	-
	Cd	4.06	42.00	13.07	-	10.21	12.20	-	-
	Cr	25.17	72.00	0.0000	-	54.48	66.21	-	-
	Cu	0.49	124.49	8.25	-	74.62	15.45	-	-
	Mn	0.0000	2036.8	850.17	-	2417.7	2719.3	-	-
	Pb	18.78	320.36	19.89	-	105.15	132.16	-	-
	THg	0.21	0.0000	0.14	-	0.15	0.11	-	-
	Zn	1379.6	12947	531.68	-	1109.9	2158.7	-	-
		N=50; Soil pH=7.3±0.04				N=50; Soil pH=6.7±0.03			
Close reference	As	3.17	3.97	0.0000	49.82	19.04	16.99	-	-
	Cd	0.97	2.99	17.47	2.90	3.91	8.11	-	-
	Cr	29.34	3.97	75.40	4.14	178.43	10.26	-	-
	Cu	265.10	68.47	94.40	0.0000	101.81	85.12	-	-
	Mn	1632.4	219.65	157.19	135.63	2646.7	1930.4	-	-
	Pb	170.18	0.0000	0.0000	14.73	50.27	41.27	-	-
	THg	0.09	0.13	0.03	0.05	0.13	0.09	-	-
	Zn	1639.0	748.39	0.0000	0.0000	733.57	665.47	-	-
		N=50; Soil pH=6.0±0.10				N=50; Soil pH=7.8±0.04			
Far reference	As	1.79	-	43.17	3.02	6.57	-	-	5.65
	Cd	19.63	-	8.65	0.0000	9.75	-	-	12.21
	Cr	9.94	-	0.0000	179.25	211.49	-	-	123.49
	Cu	122.89	-	64.21	30.34	79.74	-	-	44.40
	Mn	1701.5	-	585.27	878.08	1565.0	-	-	2045.8
	Pb	75.67	-	24.87	21.51	38.03	-	-	45.21
	THg	0.06	-	0.07	0.05	0.06	-	-	0.06
	Zn	808.54	-	614.04	527.20	477.36	-	-	581.46
		N=50; Soil pH=7.9±0.05				N=50; Soil pH=8.2±0.04			

mining could be relevant to our study because soil samples were collected at Pb–Zn mine tailings and nearby areas, inferring that the residues of the studied metals and metalloids may have originated from the same pollution source factor.

The third source factor probably represents irrigation water. This source factor was dominated by residues of Cd and THg at all three sites, As and Mn at the mine and far reference sites, Cu and Cr at both two reference sites,

and Zn as well as Pb at the far reference site, and occurred only in rice paddy agroecosystems. Arsenic in ecosystems is predominantly related to As-contaminated groundwater (Rodríguez-Lado et al., 2013). Irrigation of crops using As-contaminated surface water, as well as groundwater, is the main pollution source of As in agricultural ecosystems (Luo et al., 2021). Irrigation water is also reported to introduce other metals in agricultural soil, including Cd and Mn (Arao et al., 2009; Hou et al., 2014; Luo et al.,

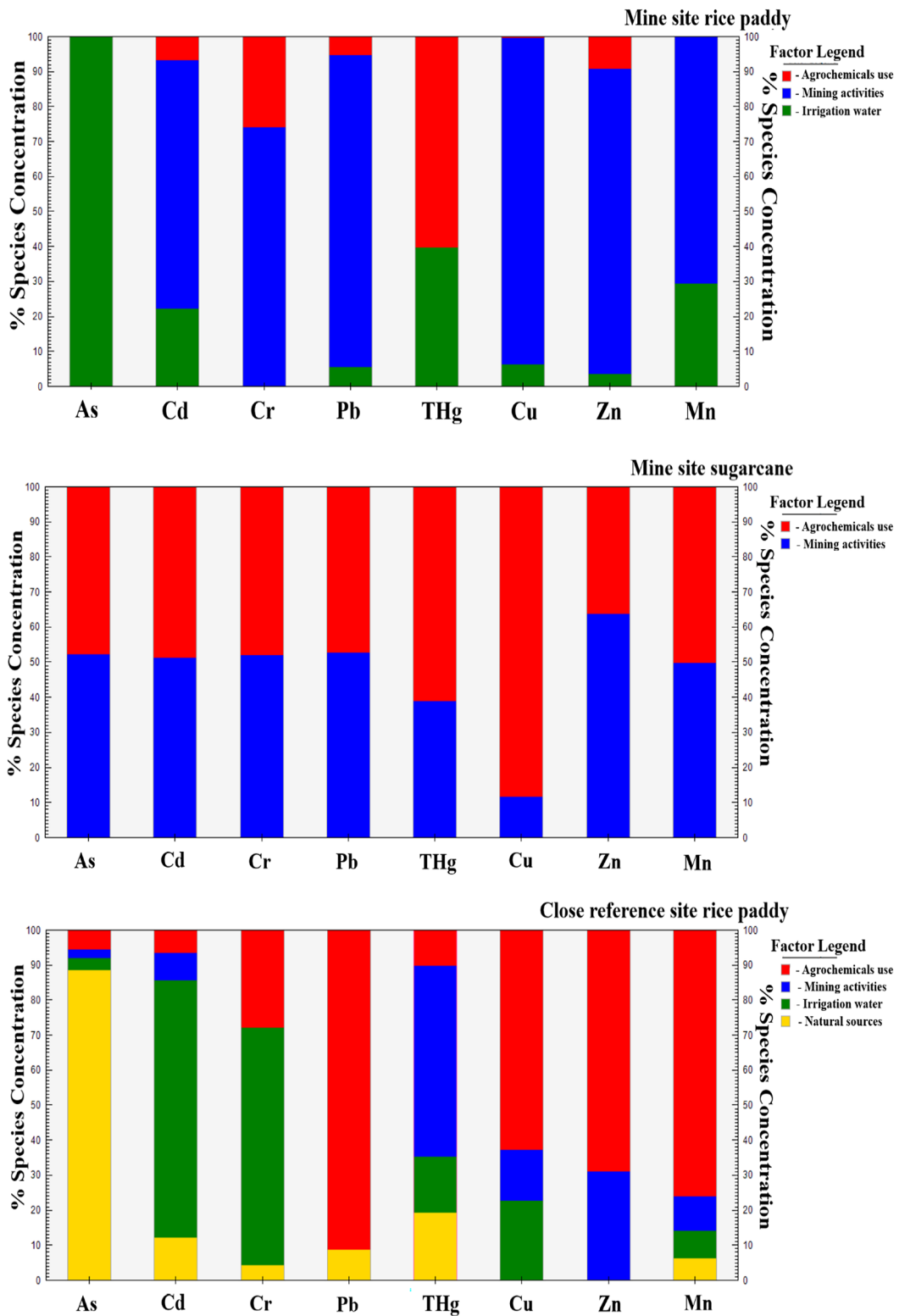


Fig. 2 Source factor contributions (%) of various metals/metalloids as estimated by the PMF model in agricultural soil samples at different sites in rice paddy and sugarcane ecosystems

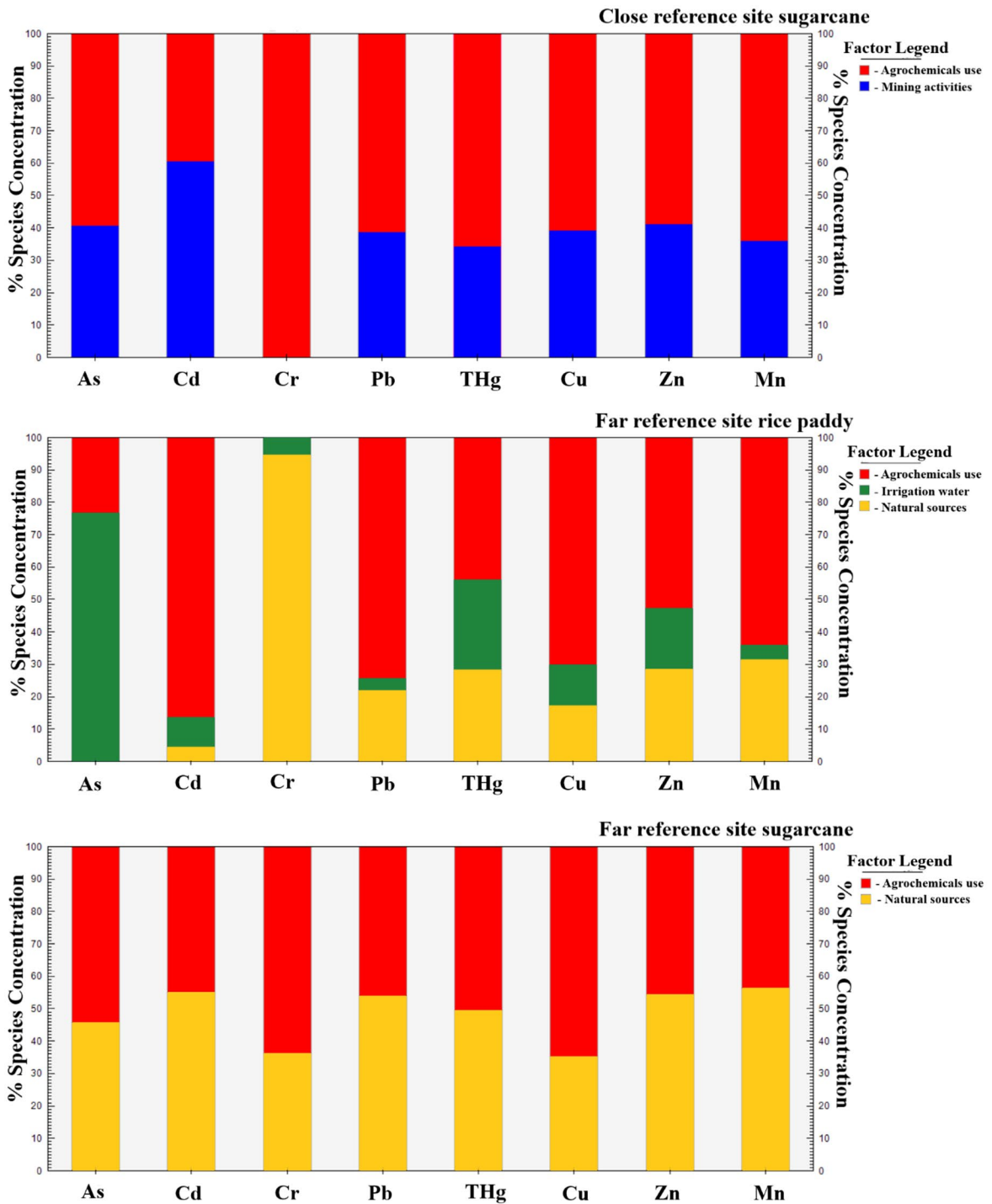


Fig. 2 (continued)

2009; Xin et al., 2011; Zhao et al., 2015), Cr (Hou et al., 2014; Huang et al., 2015; Luo et al., 2009), Cu (Hou et al., 2014; Luo et al., 2009; Xin et al., 2011), Hg, Pb, and Zn (Hou et al., 2014; Luo et al., 2009). This may well apply to our research, due to the irrigation of rice paddy agroecosystems, and lack of irrigation of sugarcane, at all sites.

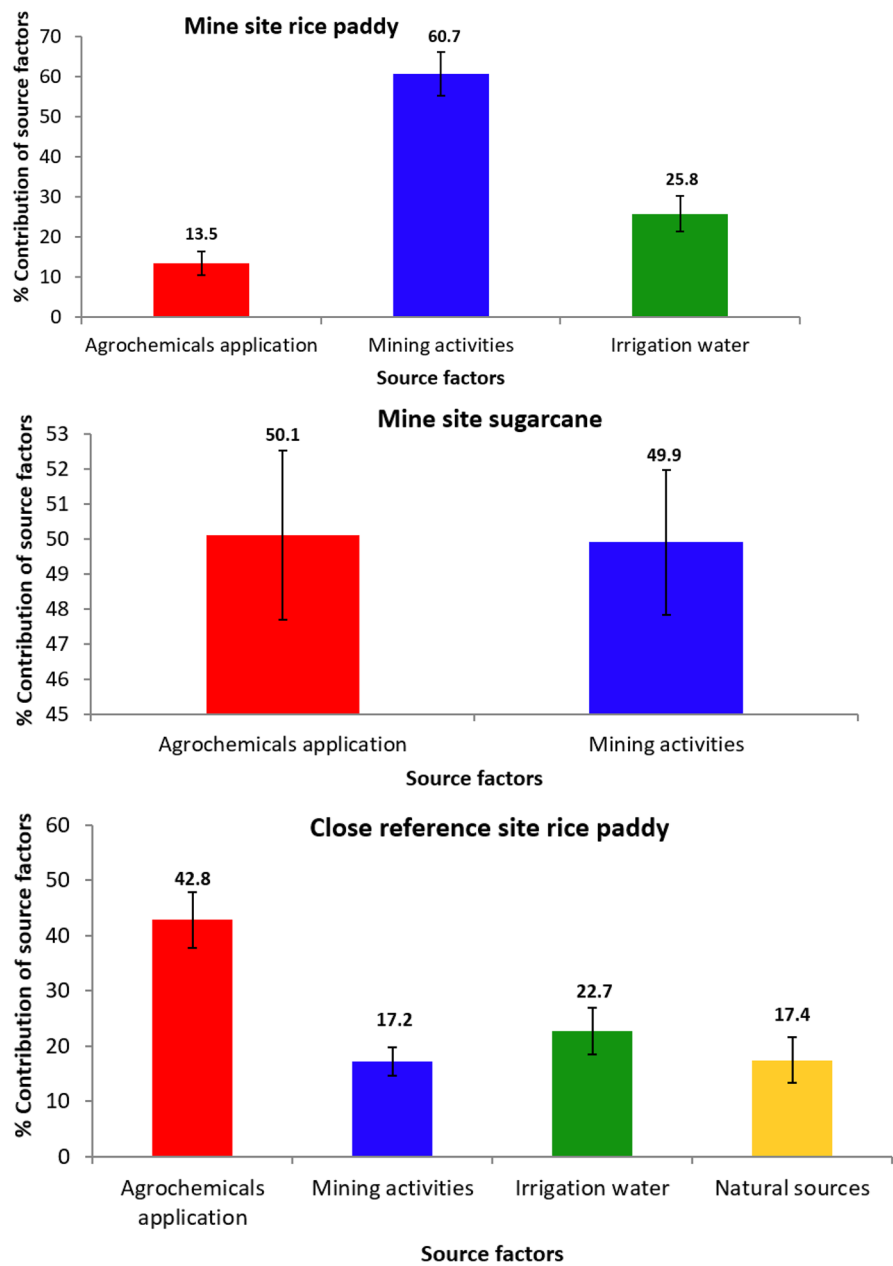
The fourth source factor is most likely signifying natural sources. In this source factor, Cr, Cu, Mn, Pb, THg, and Zn were the prominent metals at the far reference site, both in rice paddy and sugarcane ecosystems; THg residues were also found in this factor at close reference site in rice paddy ecosystem. Other dominant metals and metalloids in this source factor were Cd and As, which were observed each at the close reference site in rice paddy and at the far reference site in sugarcane ecosystems. Metals/metalloids such As, Cr, Cd, Pb, Hg, Cu, Mn, and Zn emerge within the Earth's crust, and their natural existence in soil is a result of weathering and disintegration of the parent rock materials (Nagajyoti et al., 2010). In this source factor, the average residues of Cr, Pb, THg, and Cu in Table 2 were within the range of class II benchmark values of the "Chinese Soil Quality Standards" (Table S8). Arsenic (at the close reference site in rice paddy ecosystem) and Zn (at the far reference site in both agroecosystems), to some extent, exceeded this limit, suggesting a light contamination, while Cd demonstrated severe contamination levels (Zhao et al., 2015; MEP/MLR, 2014). Regarding Mn, baseline values of this element were not stipulated in the report of MEP and MLR, but Li et al. (2007) indicated a range of Mn concentrations in agricultural soil to be 170–1200 mg/kg. Hence, based on this value, Mn residues at the close and far reference sites in rice paddy agroecosystems were within the range, while slightly exceeding this range at the far reference site in sugarcane ecosystem, again suggesting light contamination. Overall, then, natural sources were a substantial source of metals/metalloids in both agroecosystems, with the exception of the mining site, and the close reference sugarcane ecosystems, where the amount of mining contamination may have made the natural sources negligible by comparison, at least in the models deemed optimal in the PMF evaluation process.

From the results and discussion indicated above, four source factors were apportioned by the PMF model in rice paddy soil across all sites, including mining activities, agrochemical application, irrigation water, and natural sources; sugarcane was similar but without exposure

through irrigation. Cadmium, Cr, Cu, Mn, Pb, THg, and Zn appear to be sourced from agrochemical applications, mining activities, and natural sources in both rice paddy and sugarcane ecosystems; the pattern for As is similar but appears to be due to agrochemical application and mining activities mostly in sugarcane agroecosystems. In addition, contamination of all eight metals/metalloids was ascribed to irrigation water in the rice paddy ecosystem, and due to this fact, this ecosystem consistently had a more complex source apportionment (three to four sources at any one location) than sugarcane (two sources at any one location). These results were found with strong correlations (r^2 ranging from 0.5 to 0.99) between the observed and predicted concentrations (presented in Fig. S2–S7), with only a few exceptions (THg at the far reference site in rice paddy and at all three sites in sugarcane agroecosystems was deemed weak, and As at both reference sites in sugarcane ecosystems was also deemed weak). Such results suggest that the predicted metal residues in agricultural soil samples were well modeled and considerably correlated to the measured or observed values, and hence, the selected source factors may also suitably predict the concentrations of each metal/metalloid in the collected samples both in rice paddy and sugarcane ecosystems.

The overall proportions of the selected pollution source factors to the total metal/metalloid residues in agricultural soil samples as determined by the PMF model are summarized in Fig. 3. The findings revealed that among the selected pollution source factors at the mine site in rice paddy ecosystems, on average, mining activities consisted of higher contribution followed by irrigation water, and agrochemical application being the least (Fig. 3). At the close reference site in rice paddy ecosystems, agrochemical application was a predominant source followed by irrigation water, natural sources, and mining activities being the least. Furthermore, at the far reference site in rice paddy ecosystems, agrochemical application was a dominant source followed by irrigation water, and natural sources being the least. In comparison, at the mine and close reference sites in sugarcane agricultural ecosystems, on average, agrochemical application was the dominant source factor of metals/metalloids followed by mining activities. At the far reference site in sugarcane agroecosystems, agrochemical application was the main source of metals/metalloids, followed by natural sources. Therefore, these findings infer that anthropogenic activities were the dominant pollution sources of metal and

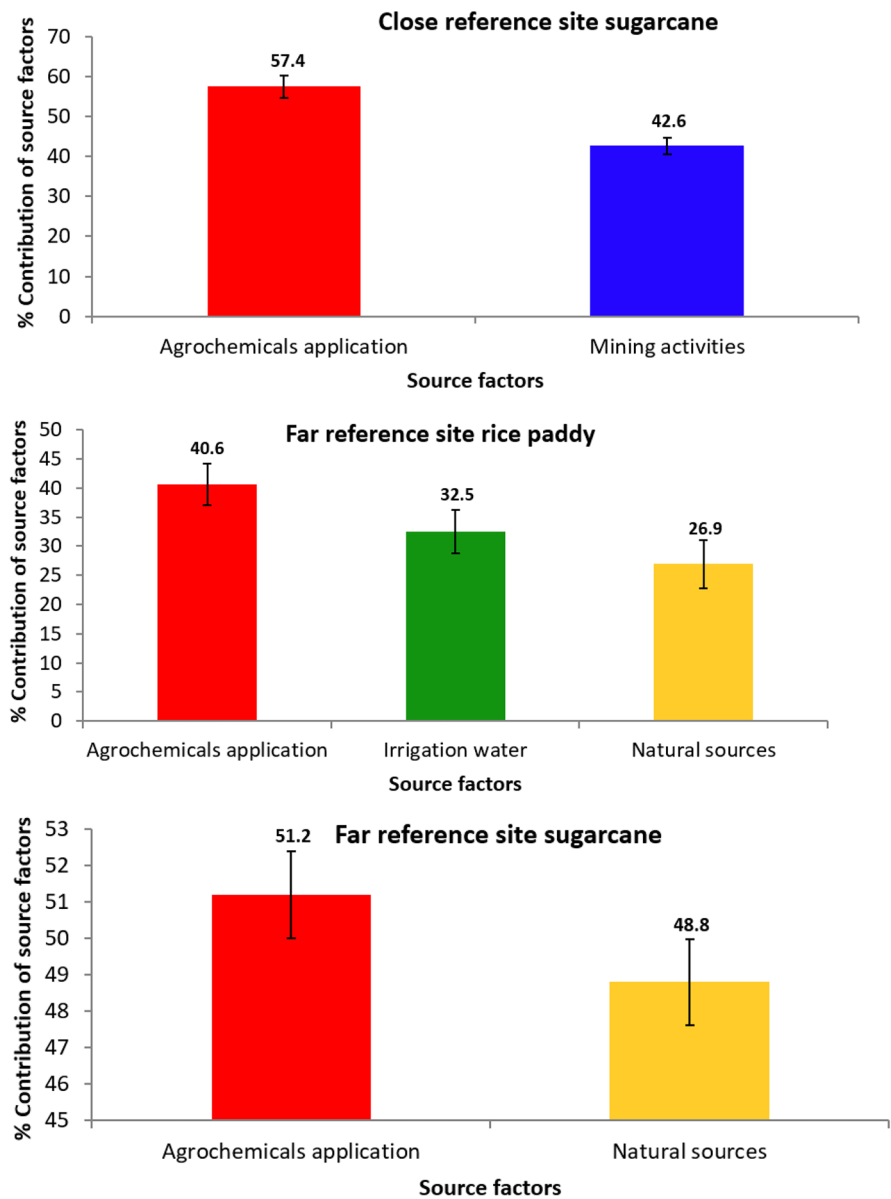
Fig. 3 Average contribution or proportion (%) of each pollution source factor to the total metal concentrations in agricultural soil samples as estimated by the PMF model



metalloid contamination both in rice paddy and sugarcane agricultural ecosystems. Despite the close reference site being situated around 6 km away from mine tailings, and there being no water connection at the surface, our results revealed mining effects to be there, too; hence,

suggesting that mining effects could lead to an extensive environmental contamination. This could be due to the influence of erosion, flooding, or leaching of metals into contaminated underground aquifers (Alloway, 2013; Kocman et al., 2013).

Fig. 3 (continued)



Conclusion and recommendation

This study aimed to identify the potential sources of metal/metalloid contamination and measure their contribution rates, comparing between rice and sugarcane agroecosystems. Relative to this objective, we found that, on average, agrochemical application was the dominant source factor of metals and metalloids both in rice paddy and in sugarcane agroecosystems at all three sites (i.e., mine, close, and far reference sites),

with one exception: at the mine site in rice paddy ecosystems, mining activity was the predominant source factor. Importantly, the PMF receptor model indicated that the optimal solution was three or four source factors for rice paddy at any one site, with four factors being involved across all sites. In comparison, there were only two source factors per site identified for sugarcane and three sources involved at all sites. Our results are thus in line with the expectation that sources of contamination would be more complicated

in rice paddy agroecosystems, which were irrigated, than sugarcane agroecosystems, which were not.

Based on our findings, we suggest the following: (1) Levels of Cd, which is highly toxic (Dragun et al., 2018; Raj & Maiti, 2020), were extremely high at the mine sites and also high relative to benchmarks at the reference sites as well (Table 1). Levels of Zn were also extremely elevated at the mine site. Hence, we suggest that agricultural and food safety authorities test farm products at the mine site, and even in the wider area, to ensure that human health is not compromised. More generally, Cd, Zn, Pb, Mn, and Cu contamination in agricultural soil is still a prevailing challenge, especially in mining areas and in agricultural fields with intensive application of fertilizers (both organic and synthetic). Therefore, it is of great importance to prioritizing the control of these metals in agroecosystems to ensure food safety, security, and human well-being. (2) Our study suggests that agrochemical input is a dominant source of exposure of metals/metalloids. Although China has banned the use of As-, Pb-, and Hg-containing pesticides in agricultural activities, there is still extensive use of approved pesticides containing other metals, particularly Cu and Zn (Luo et al., 2009). Thus, farmers should judiciously use chemical/synthetic pesticides and/or fertilizers to reduce the contamination rate of agricultural lands.

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Author contribution Wambura M. Mtemi: conceptualization, methodology, investigation, data curation, visualization, formal analysis, and writing of the original draft; Xiaohang Xu, Shilong Liu, Guangle Qiu, and Xueli Wang: methodology, software, investigation, and formal analysis; Eben Goodale and Aiwu Jiang: conceptualization, methodology, resources, supervision, and validation. All authors participated in reviewing and editing the manuscript.

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Data availability Upon acceptance, the data on the metal/metalloid residues of all soil samples will be uploaded on an online data archive (e.g., Dryad) or as supplemental data.

Declarations

Ethics approval This research does not involve human or animal subjects.

Competing interests The authors declare competing interests.

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