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Heavy Metal Accumulation in Soil-Wheat System of Coal Mining Area and Health Risk Assessment: A Case Study in Northern Anhui Province, China

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ABSTRACT

An investigation of 43 soil samples and their corresponding wheat samples collected from Qinan (QN) and Luling (LL) coal mining areas in Suzhou, China, was conducted to study the accumulation of heavy metals (Cu, Pb, Zn, Cd, Cr and Ni) in the soil-wheat system, and to evaluate the potential human health risk posed by heavy metals from long-term ingestion of local wheat. Results showed that Cu, Zn, Cd and Ni were accumulated in the soils from the two mining areas, higher proportions of all the investigated metals in residual fraction were recorded, while large amounts of Cd, Cu, Zn, Pb were also observed in the bioavailable or potential bioavailable fractions. Metal contents in the different parts of wheat mainly followed the order of Root>Stem>Grain. The trends of Bioaccumulation factor (BF) and Translocation factor (TF) values were Zn>Cd>Cu>Ni>Pb>Cr and Cu>Cd>Zn>Cr>Pb>Ni, respectively. Correlation analysis suggested that the accumulated metals in the grain were mainly supplied from exchangeable and carbonate bound fractions in soil. Since the health risk posed by heavy metals ingestion was very close to the maximum allowable limit, the safety of wheat consumption in the coal mining areas should be continually concerned.

INTRODUCTION

Heavy metals are widespread pollutants in the environment and well-known for their high toxicity, non-degradable properties and bioaccumulation. Excessive heavy metals in agricultural soil are the result of vehicular exhaust, fertilization and sewage irrigation, as well as industrial and mining activities (Yan et al. 2007). Mining of coal is an important source of heavy metal pollution in soil. It produces a large quantity of coal wastes with different composition. These materials are often deposited near coal mines and exposed to atmospheric conditions. Gradual weathering of the wastes causes the release of toxic metals into the surrounding environment. Some previous studies regarding environmental pollution in coal mining area have found significant accumulation of heavy metals in soils, dusts, sediments and vegetables (Rout et al. 2015, Zhang et al. 2016, Brandelero et al. 2017, Rai et al. 2015).

In soil-crop systems, heavy metal ions can be gradually absorbed by crop roots and then migrate upward to stems, leaves and grains, which not only represent a threat to the growth and yield of crops but also probably lead to the problem of agricultural product safety (Dong et al. 2012, Wang et al. 2017). Mobility and bioavailability of heavy metal in soil mainly depend on their specific chemical fractions rather than the total elemental contents (Baeyens et al. 2003). Based on the Tessier sequential extraction, heavy metals in soils can be classified into exchangeable (EXC), carbonate bound (CAB), Fe-Mn oxides bound (Fe-Mn), organic matter/sulphide bound (OMS) and residual (RES) fractions (Tessier et al. 1979). EXC fraction is considered to be bioavailable, CAB, Fe-Mn and OMS fractions are potentially bioavailable, while RES fraction is unavailable to plants. The occurrence and relative distribution of metals among these various fractions have been used as an important reference for understanding a metal's bioavailability in soil (Zhu et al. 2015). Besides, several studies were conducted to explore the other factors affecting heavy metals absorption by crops, including soil types, crop species and growth conditions (Wang et al. 2013, Yang et al. 2014, Khan et al. 2017).

Consumption of crop is the major route of human exposure to heavy metals (Zeng et al. 2015). Contaminated crop contains excessive essential and toxic metals, which can cause serious harmful diseases to inhabitants through the food chains. Thus, it is very essential to estimate the potential health risk posed by heavy metals from long-term ingestion of the crops grown in the contaminated areas. Research on monitoring heavy metal concentrations in wheat collected from a market in Bangladesh showed the health risk associated with wheat consumption was negligible (Ahmed et al. 2015). However, another study found significant heavy metal exposure risk for residents from the consumption of wheat grown in Huaibei, and the inhabitants in the rural area experienced higher health risk than those in the urban area (Shi et al. 2013).

Suzhou, which is located in northern Anhui province, is an important production base of agricultural grain in China and known as "Barn of Central Plains". It had a population of 1.72 million in 2017. Wheat flour is the staple food of most local residents in Suzhou, especially in rural areas. Since the 1970s, coal mining activities in Suzhou gradually increased, which also caused serious ecological environmental problems in the mining areas. The main purpose of this work was: (i) to investigate the accumulation of the selected heavy metals (Cu, Pb, Zn, Cd, Cr and Ni) in the soil-wheat system from the coal mining areas, including metal contents in soil, in chemical fractions of soil and in different parts of wheat, (ii) to examine whether metal content in wheat grain relates to metal concentration in soil or any of the chemical fractions of soil, and (iii) to estimate the potential human health risk posed by heavy metal from long-term ingestion of wheat grown in the coal mining areas.

MATERIALS AND METHODS

Study Areas and Samples Collection

The areas of field sampling in the present study are located around Qinan (QN) and Luling (LL) coal mine in the south east of Suzhou City. The region has a sub-humid monsoon climate, which is characterized by a wide seasonal variation in temperature ranging from 32°C in summer to -2°C in winter. The average annual rainfall and temperature are 890 mm and 14.4°C. The soils in these areas are mainly Yellow fluvo-aquic soil and lime concretion black soil. Suzhou is abundant in coal resources and has a long history of mining. The exploitation of QN and LL coal mine began in 2000 and 1969, respectively. At present, more than 1.5 million tons of coal can be produced annually from QN mine. Owing to the long-term exploitation, LL mine has inevitably faced the threat of resource exhaustion and is planned to be closed down in 2019.

Forty-three sampling sites of farmland were selected for the present study, twenty-one of them are located in QN coal mining area and the others are located in LL coal mining area (Fig. 1). Sampling was carried out at wheat maturity.

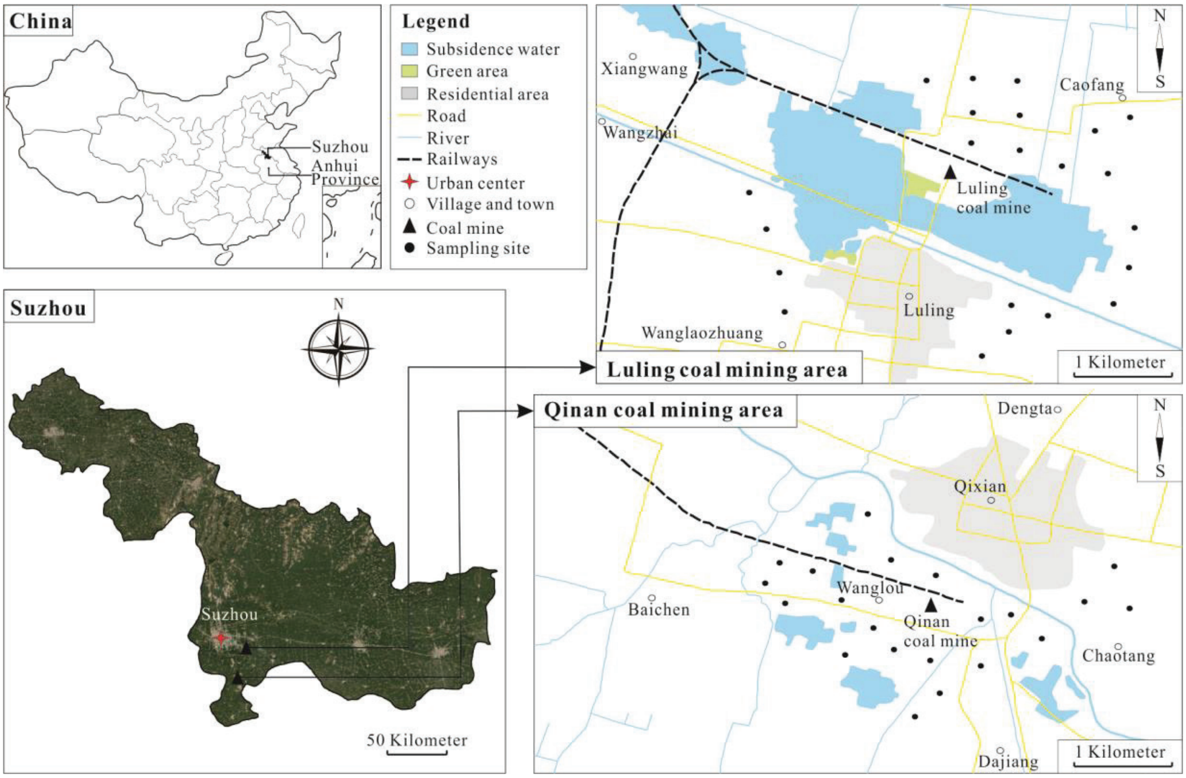

Fig. 1: Location of sampling sites in the investigated areas.

At each site, one soil sample (approximately 0.5 kg) from the 0-20 cm depth of the A horizon and its corresponding wheat sample were collected, while coordinate of sampling station was recorded with the aid of a handheld Global Positioning System (GPS). The collected samples were put into a plastic self-sealing bag and labelled before the laboratory processing.

Sample Preparation

After being transported to the laboratory, each soil sample was air-dried and then divided into two parts. One part was ground and passed through a 2-mm sieve for pH analysis, and the other part was ground with an agate mortar to pass a 0.149 mm nylon sieve for acid digestion and soil organic matter analysis. Each wheat sample was carefully cut into four parts of root, stem, leaf and grain with scissors. All the parts were thoroughly washed with running tap water to remove dirt and rinsed with deionized water three times. The cleaned roots, stems, leaves and grains were oven-dried at 80 to constant weight, then ground to powder for acid digestion.

Sample digestion: 0.2 g of each soil sample was digested with a mixture of 8 mL acids (aqua regia, $HClO_4$ and HF, 4:1:1, v/v) in a Teflon beaker and 0.50 g of each wheat sample (root, stem, leaf and grain) was also digested with a mixture of 5 mL acids (HNO_3, HCl and $HClO_4$, 5:1:1, v/v) in a glass beaker. The beakers were placed on an electric hot plate and heated at 110 for thermal decomposition of samples. After the samples were completely digested, the remaining liquid in the beakers was carefully transferred to glass volumetric flasks and diluted with MilliQ water to a final volume of 50 mL.

Chemical fraction extraction of heavy metal for soil: A five-step sequential extraction procedure (Tessier et al. 1979) was performed in this study for quantifying the contents of heavy metals in different chemical fractions in soil samples. Fraction of metal, defined by the Tessier sequential extraction method, includes five forms of exchangeable (EXC), carbonate bound (CAB), Fe-Mn oxides bound (Fe-Mn), organic matter/sulphide bound (OMS) and residual (RES). The extraction sequence, the reagents used, the extraction conditions and the extraction processes are presented in Table 1.

Analysis Methods and Quality Control

Soil pH was measured in soil-deionized water (2.5:1, v/w) suspension using a pH meter, and the content of soil organic matter was tested using the acid dichromate oxidation method (Bao 2000). The contents of heavy metals in all of the solution prepared in the above digestion and extraction procedures were determined by atomic absorption spectrophotometer (Model TAS-990FG, Purkinje General Instrument, Beijing, China).

All chemicals used in this study were of analytical grade. All the glassware, Teflon beakers and centrifuge tubes were treated with the proper cleaning procedure, including a 24 h immersion in 10% HNO_3 and thorough rinses with deionized water twice, before being used. Standard reference materials GSS-16 (GBW07430) for soil and GSB-2 (GBW10011) for

Table 1: Sequential extraction procedure of Tessier.

Extraction sequence	Extraction fraction	Reagenths	Extraction conditions	Extraction processes	Collection processes of extracts
Step 1	Exchangeable (EXC)	Solution A: 1 M $MgCl_2$	pH 7.0, 25°C	1.0 g soil sample + 8 mL solution A, shaking for 1 h continuously	**Step 1-4:** After extraction of each step, the solution was centrifuged at 3000 rpm for 20 min, the supernatant liquid was collected for analysis.
Step 2	Carbonate bound (CAB)	Solution B: 1 M NaOAc	pH 5.0, 25°C	Solid residue from step 1 + 8 mL solution B, shaking for 5 h continuously	
Step 3	Fe-Mn oxides bound (Fe-Mn)	Solution C: 0.04 M $NH_2OH{\cdot}HCl$ in 25% (v/v) HOAc	96±3°C	Solid residue from step 2 + 20 mL solution C, heating for 6 h with occasional agitation	
Step 4	Organic matter / sulphide (OMS)	(1) Solution D: 30% H_2O_2+0.02 M HNO_3 (5:3, v/v) (2) Solution E: 30% H_2O_2 (3) Solution F: 3.2 M NH_4OAc in 20% (v/v) HNO_3	(1) pH 2.0, 85±3°C (2) pH 2.0, 85±3°C 25°C	(1) Solid residue from step 3 + 8 mL solution D, heating for 2 h. (2) Then add 3 mL solution E, heating for 3 h with intermittent agitation. (3) Adding 5 mL solution F, shaking for 30 min continuously	
Step 5	Residual (RES)	Solution G: Aqua regia+ $HClO_4$+HF (4:1:1, v/v)	110°C	Solid residue from step 4 was transferred to Teflon beaker and digested with 8 ml solution G	**Step 5:** After the solid residue was completely digested, the remaining liquid in Teflon beaker was carefully transferred to glass volumetric flasks and diluted with MilliQ water to a final volume of 50 ml for analysis.

wheat were used to check the analytical accuracy of metal concentration in the experimental procedure. The recoveries of Cu, Pb, Zn, Cd, Cr and Ni in the reference materials were in the range of 84-112%. Additionally, the standard was tested repeatedly after every ten samples to check the reproducibility.

Bioaccumulation Factor and Translocation Factor

To evaluate the uptake efficiency of heavy metal by wheat, Bioaccumulation factor (BF) index of the root was adopted. It is defined as the ratio of the heavy metal concentration of wheat root to the corresponding soil. The following equation was used for the calculation.

$$BF = \frac{C_{root}}{C_{soil}} \quad \ldots(1)$$

Where C_{root} (mg·kg^{-1}) and C_{soil} (mg·kg^{-1}) are the concentrations of heavy metal in wheat root and in soil on the basis of dry weight, respectively.

Translocation factor (TF) index reflects the ability that transports the metal ion from plant root upward to other parts. In this study, the wheat root-to-grain TF was adopted and calculated as follows:

$$TF = \frac{C_{grain}}{C_{soil}} \quad \ldots(2)$$

Where C_{grain} (mg·kg^{-1}) is the concentration of heavy metal in wheat grain based on the dry weight.

Health Risk Assessment Model

To estimate the potential health risk posed by heavy metals from long-term ingestion of wheat grown in the coal mining areas, chronic daily intake (CDI) and hazard quotients (HQ) were calculated for quantifying the adverse health effects. Chronic daily intake (CDI) is the exposure to the population expressed as the mass of a substance per unit body weight per unit time averaged over a long period (a lifetime) (Garg et al. 2014). It can be calculated by the following equation:

$$CDI = \frac{C_{grain} \times IR \times EF \times ED}{BW \times AT} \quad \ldots(3)$$

Where IR (kg·person·d^{-1}) is the daily wheat flour intake rate. According to the data provided by the Statistical Bureau of China, IR values in this study are 0.143 and 0.052 kg·person·d^{-1} for adults and children, respectively. EF is the exposure frequency (350 d·year^{-1}), ED (year) is the exposure duration, in this study of 30 years for adults and 6 years for children. BW (kg) is the average weight of residents, in this study, of 61.6 kg for adults and 18.6 kg for children. AT is the average exposure time for non-carcinogens (E_D×365 days)

Hazard quotients (HQ) is defined as the ratio of the estimated daily intake of metals and the oral reference dose (Rfd). It is calculated following the formula established by the US Environmental Protection Agency (US EPA 2011).

$$HQ = \frac{CDI}{RfD} \quad \ldots(4)$$

Where RfD represents the maximum oral dose level without any appreciable risk, and its values for Cu, Pb, Zn, Cd, Cr and Ni are 4.0×10^{-2}, 3.5×10^{-3}, 3.0×10^{-1}, 1.0×10^{-3},1.50 and 2.0×10^{-2} mg·kg^{-1}·day^{-1}, respectively (US EPA 2009).

To assess the overall potential health risks posed by more than one metal, hazard index (HI) was calculated as the sum of the HQs due to individual metal in wheat grain (Garg et al. 2014), as described in the following equation:

$$HI = HQ_1 + HQ_2 + \cdots\cdots + HQ_n \quad \ldots(5)$$

If HI≤1.0, there will be no obvious adverse effects through wheat ingestion, whereas a HI>1.0 indicates that potential risk for wheat ingestion is possible (Xue et al. 2012).

Data Statistics

Data statistics were performed by SPSS 13.0 software package, and all figures in this article were produced by CorelDRAW 12.0. Pearson correlation coefficients were calculated to identify the relationships between metal content in wheat grain and total metal concentration in soil, as well as between metal content in wheat grain and metal content in any of the chemical fractions.

RESULTS AND DISCUSSION

Physico-Chemical Properties and Heavy Metal Contents in Soil

The statistical characteristics of physico-chemical properties and metal concentrations in soils collected from QN and LL mining areas are given in Table 2. Soils in the investigated areas were slightly acidic and had mean pH values of 6.87 in QN and 6.58 in LL. Compared with "the classification criterion of soil nutrients based on the second soil survey of China", the organic matter content was in the lacking level. In the two mining areas, higher Cd contamination than the other metals in soil was observed. The mean Cd concentrations in QN (0.381 mg·kg^{-1}) and LL (0.421 mg·kg^{-1}) were 1.27 and 1.40 times higher than the environmental quality standard for agricultural soil in China (GB15618-2018), while mean concentrations of the other metals were all lower than the

Table 2: Descriptive statistics of physico-chemical properties and heavy metal concentrations in soil.

		pH	Organic matter ($g{\cdot}kg^{-1}$)	Cu ($mg{\cdot}kg^{-1}$)	Pb ($mg{\cdot}kg^{-1}$)	Zn ($mg{\cdot}kg^{-1}$)	Cd ($mg{\cdot}kg^{-1}$)	Cr ($mg{\cdot}kg^{-1}$)	Ni ($mg{\cdot}kg^{-1}$)
QN (n=21)	Max.	8.19	18.06	50.51	59.73	106.44	0.813	108.75	100.14
	Min.	5.53	3.27	12.63	16.81	48.68	0.159	43.42	28.62
	Mean	6.87	11.42	26.60	26.88	73.39	0.381	70.73	39.81
	Stdev.	1.05	5.14	10.15	9.57	17.43	0.174	16.89	16.89
	C.V.(%)	15.30	45.01	38.15	35.59	23.75	45.89	23.88	37.24
LL (n=22)	Max.	8.13	19.22	49.66	39.25	113.04	0.775	80.80	79.84
	Min.	5.17	3.10	13.36	14.73	43.35	0.126	49.11	26.03
	Mean	6.58	10.77	31.71	27.83	72.47	0.421	65.24	42.26
	Stdev.	0.98	5.55	8.23	5.42	16.94	0.120	10.02	10.42
	C.V.(%)	14.92	51.48	25.96	19.49	23.37	28.44	15.36	24.65
Environmental Standard for Agricultural soils in China (GB15618-2018)		-	-	100	120	250	0.3	200	100
Anhui Background		-	-	20.4	26.6	62.0	0.097	67.5	29.8

standard. But when compared to the background values of Anhui province in China, mean concentrations of Cu (26.60 $mg{\cdot}kg^{-1}$ in QN and 31.71 $mg{\cdot}kg^{-1}$ in LL), Zn (73.39 $mg{\cdot}kg^{-1}$ in QN and 72.47 $mg{\cdot}kg^{-1}$ in LL), Cd and Ni (39.81 $mg{\cdot}kg^{-1}$ in QN and 42.26 $mg{\cdot}kg^{-1}$ in LL) were higher, while Pb (26.88 $mg{\cdot}kg^{-1}$ in QN and 27.83 $mg{\cdot}kg^{-1}$ in LL) was slightly higher, indicating that noticeable metal accumulations in soils had emerged and were very likely to be caused by the intensive mining activities in the investigated areas.

Compared with QN area, the mean concentrations of Cu, Pb, Cd and Ni in soils from LL area were higher, while the mean concentrations of Zn and Cr were slightly lower. Additionally, Coefficients of Variation (C.V.) of the six heavy metals in LL area were all lower than that in QN area, proving that the spatial distribution of heavy metal contents in soils around LL mine was more uniform. The difference between the two mining areas might be due to their different mining duration. LL mine is an old coal mine with a mining history of nearly 50 years, the long-term anthropogenic disturbance and impacts of natural factors in this mining area have not just resulted in the accumulative effect of toxic metals in the soil environment, but intensified the migration and diffusion

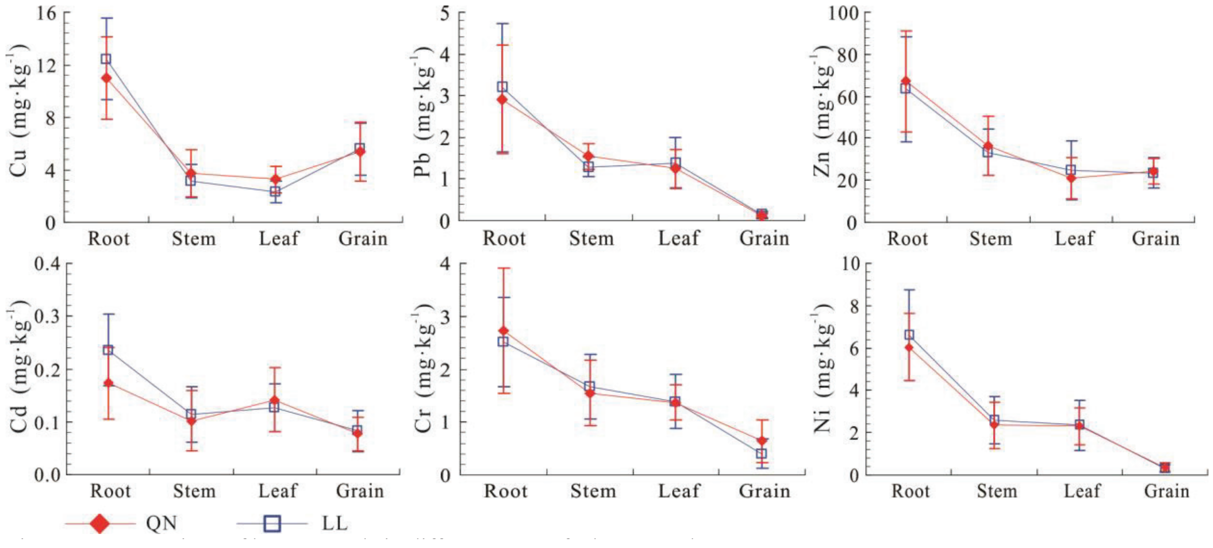

Fig. 2: Concentrations of heavy metals in different parts of wheat samples.

of pollutants as well, thus leading to the more uniform spatial distribution of soil contamination in the mining area.

Chemical Fraction of Heavy Metals in Soil

The concentrations and percentage of heavy metals present in the various fractions are given in Table 3. For further examining the accuracy of analytical results obtained from sequential extraction procedure in this study, an internal check was carried out by comparing the sums of metal concentrations in all the five fractions with the total metal concentrations in soils obtained from acid digestion. Metal recoveries were calculated by the following equation and the results are also presented in Table 3.

$$\text{Recovery} = \frac{EXC + CAB + Fe\text{-}Mn + OMS + RES}{C_{soil}} \times \mathbf{100\%} \quad \ldots(6)$$

As given in Table 3, the values of metal recoveries in the two mining areas ranged from 89.9-108.1%, so it can be concluded that the results obtained from sequential extraction were in good agreement with those by digestion.

The bioavailability and ecotoxicity of heavy metals are mainly related to their chemical fractions. Metals in EXC fraction are weakly sorbed on the soil surface by electrostatic interaction and could be easily released by ion exchange processes (Kumar & Ramanathan 2015, Barać et al. 2016).

Table 3: Concentrations and percentages of heavy metals in the five fractions.

		EXC	CAB	Fe-Mn	OMS	RES	Sum	Recovery (%)
***QN are*a**								
Cu	Content (mg·kg^{-1})	0.97±0.36	4.19±1.95	3.24±2.66	6.12±2.73	10.23±3.91	24.75	93.1
	Percentage (%)	3.92±1.45	16.93±7.88	13.09±10.75	24.73±11.03	41.33±15.8		
Pb	Content (mg·kg^{-1})	2.57±1.08	3.44±1.54	10.24±3.55	3.53±1.62	8.65±7.04	28.43	105.8
	Percentage (%)	9.04±3.8	12.13±5.45	36.01±12.45	12.41±5.7	30.41±24.75		
Zn	Content (mg·kg^{-1})	5.42±1.50	15.29±4.68	11.35±3.42	7.94±2.16	30.71±9.53	70.71	96.3
	Percentage (%)	7.67±2.12	21.62±6.62	16.05±4.84	11.23±3.05	43.43±13.48		
Cd	Content (mg·kg^{-1})	0.070±0.031	0.083±0.038	0.061±0.040	0.019±0.014	0.156±0.130	0.389	102.0
	Percentage (%)	18.12±8.03	21.32±9.71	15.57±10.32	4.88±3.61	40.10±33.51		
Cr	Content (mg·kg^{-1})	1.09±0.33	2.01±0.76	2.37±0.49	4.07±1.92	64.17±17.37	73.70	104.2
	Percentage (%)	1.48±0.45	2.73±1.03	3.22±0.66	5.52±2.6	87.06±23.57		
Ni	Content (mg·kg^{-1})	3.59±1.14	4.42±1.95	3.53±1.40	5.10±2.38	26.41±9.56	43.05	108.1
	Percentage (%)	8.34±2.65	10.27±4.53	8.2±3.25	11.85±5.53	61.35±22.21		
***LL are*a**								
Cu	Content (mg·kg^{-1})	1.14±0.44	4.87±8.52	3.56±1.81	7.36±2.30	13.96±5.45	30.89	97.4
	Percentage (%)	3.69±1.42	15.77±27.58	11.52±5.86	23.83±7.45	45.19±17.64		
Pb	Content (mg·kg^{-1})	2.91±1.03	4.06±1.48	9.64±3.28	4.35±1.77	8.90±4.73	29.86	107.3
	Percentage (%)	9.74±3.41	13.59±4.95	32.27±10.98	14.6±5.93	29.8±15.84		
Zn	Content (mg·kg^{-1})	4.90±1.24	16.26±6.28	11.88±4.62	7.37±1.78	24.73±7.59	65.14	89.9
	Percentage (%)	7.52±1.92	24.96±9.64	18.24±7.09	11.31±2.75	37.96±11.65		
Cd	Content (mg·kg^{-1})	0.087±0.030	0.099±0.031	0.067±0.022	0.014±0.004	0.127±0.106	0.394	93.6
	Percentage (%)	22.01±7.51	25.12±7.89	17.00±5.50	3.56±0.98	32.31±26.97		
Cr	Content (mg·kg^{-1})	1.01±0.28	1.64±0.80	2.01±0.57	3.70±1.55	57.25±9.47	65.61	100.6
	Percentage (%)	1.54±0.43	2.5±1.22	3.06±0.87	5.64±2.36	87.26±14.43		
Ni	Content (mg·kg^{-1})	3.25±1.09	3.72±1.62	2.96±0.50	5.14±1.97	26.30±7.45	41.37	97.9
	Percentage (%)	7.86±2.63	8.99±3.92	7.15±1.21	12.42±4.76	63.57±18.01		

Sum = EXC+CAB+Fe-Mn+OMS+RES

Among the six metals in this study, Cd showed the highest percentage (18.12% in QN and 22.01% in LL) in EXC fraction, while Cr occupied the lowest EXC fraction as only 1.48% in QN and 1.54% in LL. The percentages of Pb, Zn and Ni in EXC fraction seemed to have a slight difference (7-10%).

In CAB fraction, the proportional distribution was in the order of Cd≈Zn>Cu>Pb>Ni>Cr. Over 20% of Cd and Zn were found in CAB fraction, implied that Cd and Zn are more inclined to be associated with carbonate minerals. This finding is consistent with the result of the previous research (Barać et al. 2016). A possible explanation for this is that Cd and Zn have an ionic radius similar to that of Ca, so they could easily substitute the Ca ions in calcium carbonate in the soils and co-precipitate with the carbonates.

Metals bounded by Fe-Mn oxides in soil have potential activity and can be released in reducible conditions. In the Fe-Mn fraction, the largest percentage was observed for Pb, in comparison with the other metals. Pb also dominantly existed in the third fraction, with the mean percentage values of 36.01% in QN and 32.27% in LL, while a considerable amount of Zn (16.05% in QN and 18.24% in LL) and Cd (15.57% in QN and 17.00% in LL) were also found in this fraction. Previous studies concerned with soil have observed high proportions of Pb and Zn in Fe-Mn fraction (Jalali & Hemati 2013, Li et al. 2015). However, the high proportion of Cd in this fraction is rarely reported. The strong associations between Cd and the Fe-Mn oxides may be related to the redox condition in the soil. Under the influence of mining activities, a large number of SO_4^{2-}, originating from colliery wastewater and leaching solution of coal gangue, were discharged into the soils in the mining area. SO_4^{2-} is an important oxidant in soil, and its massive accumulation will result in the raising of oxidation-reduction potential (ORP) values, which are highly favourable for the association between the Fe-Mn oxides and some metal ions, such as Pb, Cd and Zn. A previous study also found that Cd contents in Fe-Mn fraction increased when a certain amount of Na_2SO_4 was added into the soil (Li et al. 2017).

Heavy metals associated with OMS fraction are ordinarily considered to be relatively stable under normal soil conditions, but the degradation of organic matter under oxidizing conditions can lead to the release of soluble metals bound to those materials (Bakircioglu et al. 2011). In this fraction, the proportional distribution was in the order of Cu>Pb>Ni>Zn>Cd>Cr. A relatively large amount (more than 20%) of Cu associated with OMS fraction was observed in this study. This suggested that quite a few Cu ions in soil probably exist in the form of organically complexed metal species, and may be because Cu has a high affinity to some natural organic matters, such as humic substances (Pempkowiak et al. 1999).

Generally, RES fraction is considered to be unavailable and metals in this fraction are securely fixed in the crystal of minerals (Ashraf et al. 2012). In this study, almost all the investigated metals, except Pb, were dominantly associated with RES fraction in soil. Cr occupied the largest RES fraction in both QN (87.06%) and LL (87.26%) areas, followed by Ni (61.35% in QN and 63.57% in LL), indicating that the two metals in soils from the investigated areas could hardly be released under natural condition.

Heavy Metal Concentrations in Different Parts of Wheat

Heavy metal concentrations in different parts of wheat samples are illustrated in Fig. 2. The distribution of most metals in wheat occurred in the following order: Root>Stem>Grain, only with an exception of Cu, of which concentration in grain was higher than those in the stem. Mean concentrations of Cu, Pb, Zn, Cd, Cr and Ni in the roots, of 11.01, 2.92, 67.17, 0.17, 2.73 and 6.04 mg·kg^{-1} in QN area and of 12.43, 3.19, 63.33, 0.24, 2.52 and 6.61 mg·kg^{-1} in LL area, were much higher than those in the aboveground organs, showing that these metals are mainly trapped by roots after being assimilated, and only a few of them can be transported to other organs of wheat. This is also considered to be an adaptive strategy of wheat under the adverse conditions for avoiding toxic

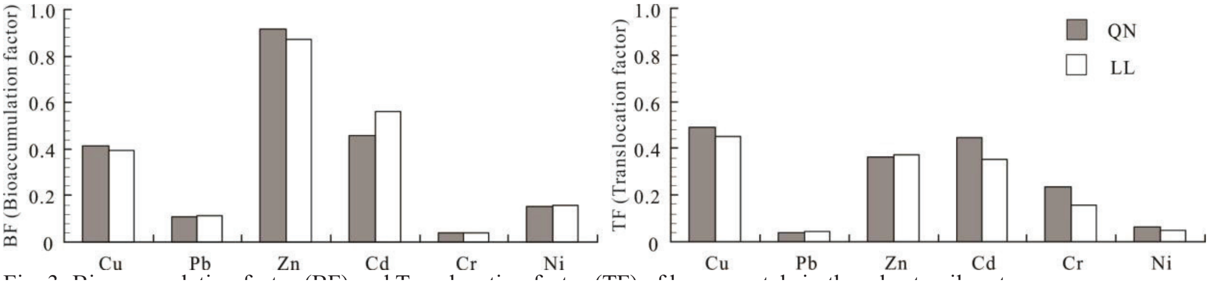

Fig. 3: Bioaccumulation factor (BF) and Translocation factor (TF) of heavy metals in the wheat-soil system.

hazards of heavy metals to photosynthesis and metabolism (Khan et al. 2015). Cd in leaves in the two mining areas and Pb in leaves in LL area were slightly higher than those in stems, the other metals in leaves showed the approximately equal concentrations or slightly lower concentrations to than those in stems. Compared with the existing standards applied to food safety in China (Table 4), the mean concentrations of all six metals in grains were below the tolerance limits. Nevertheless, not all the samples were in the safe range. The numbers of sample exceeding the tolerance limits of Pb, Cd and Cr accounted for 14.3%, 33.3% and 19.0% in QN area, and 18.2%, 22.7% and 4.5% in LL area, respectively. It can be seen from the above data that Cd pollution in wheat grains was relatively more common in the investigated areas, which coincides with the high total Cd content in the soils.

As wheat absorbs heavy metals in soils mainly through the roots and then migrate to other parts of the plant (Dong et al. 2012), it is necessary to evaluate the absorbing capacity of roots and transporting capacity from root to grain. The mean values of BF and TF for Cu, Pb, Zn, Cd, Cr and Ni in the soil-wheat system are shown in Fig. 3. The trend of mean BF values of heavy metals was Zn>Cd>Cu>Ni>Pb>Cr, while mean TF values followed the order of Cu>Cd>Zn>Cr>Pb>Ni. These trends are consistent with the result obtained from the laboratory pot experiments of wheat (Skiba & Wolf 2017), and similar to the data obtained from a case study of wheat grown on sewage irrigated soils (Meng et al. 2016). Higher BF and TF values for Cu, Zn and Cd observed in this study indicated that wheat plants from the investigated areas are more efficient uptakers of these metals, and this might be related to the active absorption and transport of the three trace elements by wheat. As the essential nutrient elements for plant growth and for synthesizing of some important enzymes, Cu and Zn are widely involved in various physiological activities of the plant. Therefore, the two metals can be actively absorbed and transferred by the plant during the metabolic processes. Though Cd is the non-essential element of plant, the similarities of ionic radius and valence between Cd^{2+} and Ca^{2+}, as well as Zn^{2+}, enable Cd^{2+} ions to combine with enzymes in place of Ca^{2+} and Zn^{2+}, and also to be transferred to plant cells through the channels of Ca^{2+} and Zn^{2+} (Gu et al. 2005, Wang et al. 2017).

Table 4: Tolerance limits (Chinese standard) of heavy metals in wheat grain, as well as the numbers and percentages of wheat sample exceeding the standards in this study.

	Tolerance limits (mg·kg^{-1})	QN (n=21)			LL (n=22)		
		Metal contents in grain (mg·kg^{-1})	Sample numbers exceeded standards	Percent exceeded standards(%)	Metal contents in grain (mg·kg^{-1})	Sample numbers exceeded standards	Percent exceeded standards(%)
Cu	10[a]	5.38±2.23	0	0	5.60±1.97	0	0
Pb	0.2[b]	0.12±0.06	3	14.3	0.15±0.07	4	18.2
Zn	50[a]	24.23±6.08	0	0	23.45±7.31	0	0
Cd	0.1[b]	0.077±0.032	7	33.3	0.083±0.039	5	22.7
Cr	1.0[b]	0.64±0.41	4	19.0	0.40±0.28	1	4.5
Ni	1.0[b]	0.37±0.20	0	0	0.31±0.16	0	0

a: Chinese Agricultural Standard for wheat (NY861-2004). b: Chinese Hygiene Standard for wheat (GB2762-2012).

Table 5: Pearson correlation coefficients between the metal contents in wheat grains and those in any of the chemical fractions of soils, as well as total metal contents of in soils (n=43).

Element	Metal fraction					Total concentration in soil
	EXC	CAB	Fe-Mn	OMS	RES	
Cu	0.464**	-0.173	0.035	0.374*	0.055	0.166
Pb	0.330*	0.508**	0.057	-0.056	0.125	0.321*
Zn	0.034	-0.034	-0.123	0.161	0.095	0.056
Cd	0.540**	0.559**	0.318*	0.126	0.008	0.459**
Cr	0.434**	0.365*	-0.337*	-0.029	-0.053	-0.046
Ni	0.709**	0.475**	-0.120	0.373*	0.053	-0.002

*Correlation is significant at 95% confidence level (n=43, $r_{critical}$=0.301); **Correlation is significant at 99% confidence level (n=43, $r_{critical}$=0.389).

Correlation Analysis

To investigate whether the metal content in wheat grain relates with that in soil or any of the chemical fractions, correlation analysis was performed based on testing data of the 43 soil and wheat samples collected from the two mining areas, and the results are given in Table 5. The correlation between grain metals and total soil metals for Cd was very significant (R=0.459), and for Pb was significant (R=0.321), whereas for Cu, Zn, Cr and Ni were insignificant, suggesting that total contents of heavy metals in soil, except Cd and Pb, could hardly be the adequate indicators for metal uptake by wheat.

Most of the metals in wheat grains had the strongest correlations with those in EXC fraction or CAB fraction, which showed that the accumulated metals in grain were mainly supplied from the two fractions, or one of the two fractions in soil. For example, grain-Cu correlated with EXC-Cu very significantly (R=0.464), grain-Cd correlated with EXC-Cd (R=0.540) as well as CAB-Cd (R=0.559) very significantly. An exception of the relationship was for grain-Zn, which had a very low correlation with any of the fractions extracted by Tessier procedure, and it might be associated with the disturbance to Zn contents in various chemical fractions in soils caused by frequent and repeated applications of Zn fertilizer in the investigated areas. The correlations between metals in wheat grain and those in RES fraction were all insignificant, reconfirming the view that metals in RES fraction are unlikely to be absorbed by the plant (Bakircioglu et al. 2011). Furthermore, significant positive correlations were also observed between grain-Cd and Fe-Mn-Cd (R=0.318), grain-Cu and OMS-Cu (R=0.374), and grain-Ni and OMS-Ni (R=0.373), revealing that Cu and Ni in OMS fraction and Cd in Fe-Mn fraction were important sources of the accumulated metals in wheat grain.

Risk Assessment

Based on the mean concentrations of Cu, Pb, Zn, Cd, Cr and Ni in wheat grains from the investigated mining areas, chronic daily intake (CDI), hazard quotient (HQ) and hazard index (HI) of heavy metals by consumption of wheat were calculated and listed in Table 6. In the two mining areas, the CDI values of heavy metals for adult and children followed the identical order of Zn>Cu>Cr>Ni>Pb>Cd, which was similar to the result of a previous study in Tianjin sewage irrigation area (Zeng et al. 2015). Children had higher CDI values of each metal than adults.

HQ values of the studied metals for both adults and children showed the following decreasing order of Cu>Zn>Cd>Pb>Ni>Cr in QN area, and of Cu>Cd>Zn>Pb>Ni>Cr in LL area. All the metals in this study had the HQ values far below 1.0, and Cu reached the highest value of 0.377 for children in LL area. Therefore, it can be deduced that intake of a single metal through wheat consumption in mining areas could not cause an obvious adverse effect on human health. The data in the present study were higher than the HQ values of wheat in the irrigated area of Jinghui in China (Lei et al. 2015) and those of wheat from the markets of Bangladesh (Ahmed et al. 2015), but lower than the results obtained from metal mining areas, where several studies showed the HQ values far above 1.0 (Lim et al. 2008, Du et al. 2018).

As given in Table 6, the HI values for adults and children in QN area were 0.771 and 0.931, slightly lower than those (0.801 and 0.968) in LL area. It seemed that children were more susceptible to heavy metal exposure through local wheat consumption than adults, and the consistent results were reported by other scholars (Si et al. 2014, Zota et al. 2011). In both the mining areas, Cu, Zn and Cd made important contributions to the calculated HI values, which

Table 6: Chronic daily intake (CDI), hazard quotient (HQ) and hazard index (HI) for heavy metals by consumption of wheat grain around the two coal mining areas.

	QN				LL			
	Adult		Children		Adult		Children	
	CDI ($mg \cdot kg^{-1} \cdot d^{-1}$)	HQ	CDI ($mg \cdot kg^{-1} \cdot d^{-1}$)	HQ	CDI ($mg \cdot kg^{-1} \cdot d^{-1}$)	HQ	CDI ($mg \cdot kg^{-1} \cdot d^{-1}$)	HQ
Cu	1.20×10^{-2}	0.300	1.45×10^{-2}	0.363	1.25×10^{-2}	0.312	1.51×10^{-2}	0.377
Pb	2.64×10^{-4}	0.075	3.19×10^{-4}	0.091	3.26×10^{-4}	0.093	3.94×10^{-4}	0.112
Zn	5.41×10^{-2}	0.180	6.53×10^{-2}	0.218	5.23×10^{-2}	0.174	6.32×10^{-2}	0.211
Cd	1.72×10^{-4}	0.172	2.08×10^{-4}	0.208	1.86×10^{-4}	0.186	2.24×10^{-4}	0.224
Cr	1.42×10^{-3}	0.001	1.72×10^{-3}	0.001	8.90×10^{-4}	0.001	1.07×10^{-3}	0.001
Ni	8.36×10^{-4}	0.042	1.01×10^{-3}	0.051	6.97×10^{-4}	0.035	8.42×10^{-4}	0.042
HI		0.771		0.931		0.801		0.968

coincides with the high BF and TF values of the three metals in soil-wheat system mentioned before (Fig. 3). Although there was insignificant health risk through ingestion of wheat grown in the mining areas because all the HI values calculated in this study were below 1.0, it should be also noticed that the HI values for local residents, especially for children, were very close to 1.0, which suggested that more attention should be continually paid to the safety of wheat consumption in the coal mining areas.

CONCLUSIONS

The mean concentrations of Cu, Zn, Cd and Ni in soil from the investigated areas were higher than the background values of Anhui province. In particular, Cd concentration was higher than the environmental quality standard for agricultural soil in China (GB15618-2018). Compared with QN mine, LL mine had a longer mining duration, which caused relativity more uniform spatial distribution of heavy metals in soils around this mine. Chemical fraction analysis reflected that Cu, Zn, Cd, Cr and Ni dominantly existed in RES fraction, while Pb mainly existed in both Fe-Mn and RES fractions. Considerable amounts of Cd were observed in EXC, CAB and Fe-Mn fractions, a high percentage of Zn were also found in CAB and Fe-Mn fractions, while over 20% of Cu was detected in OMS fraction. Cr and Ni were most stable in soil because over 60% of them were associated with RES fraction. Heavy metals, except Cu, in the different parts of wheat, followed the order of root>stem>grain, and mean concentration of all the six metals in grains were below tolerance limits of the existing standards in China. Higher BF and TF values for Cu, Zn and Cd were observed in this study, showing that the wheat plants from the investigated areas are more efficient uptakers of these metals. Correlation analysis suggested that EXC and CAB fractions were the dominant sources of the metals accumulated in grain, followed by Fe-Mn and OMS fractions. Furthermore, although high health risk posed by heavy metals from ingestion of wheat grown in the mining areas was not observed, all the HI values calculated in this study were very close to the maximum allowable limit of risk (1.0), which suggested that the safety of wheat consumption in the coal mining areas should be still continually concerned.

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