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Spatial Distribution and Risk Assessment of Heavy Metals in Paddy Soils of Yongshuyu Irrigation Area from Songhua River Basin, Northeast China

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Abstract: There is an increasing concern for potentially hazardous metals pollution, which can threaten crops production and human health. In this study, the spatial distribution and environmental risks of eight heavy metals in surface soil samples collected from the paddy fields in Yongshuyu irrigation area, Northeast China were investigated. The mean concentrations of Pb, Cr, Cu, Ni, Zn, Cd, Hg and As were 34.6 ± 4.67, 82.8 ± 9.51, 17.3 ± 4.09, 21.2 ± 12.0, 88.6 ± 17.9, 0.18 ± 0.15, 0.22 ± 0.07 and 8.77 ± 2.47 mg/kg, respectively, which were slightly higher than their corresponding background values of Jilin Province, indicating enrichment of these metals in the paddy soils, especially for Ni, Cd and Hg. The spatial distribution of heavy metals was closely correlated with local anthropogenic activities, such as agricultural production, mining and transportation. The hot-spot areas of As and Cd were mainly concentrated in the up-midstream where were associated with agricultural activities. Cr and Cu showed similar spatial distributions with hot-spot areas distributed the whole irrigation area uniformly. Ni was mainly distributed in the downstream where Ni quarries concentrated, while the spatial distribution patterns of Hg was mainly located in the upstream and downstream where the soil was significantly influenced by irrigation and coal mining emission. The spatial distributions of Pb and Zn were mainly concentrated along the highway side. The pollution levels of Yongshuyu irrigation area were estimated through index of geo-accumulation (I_{geo}), Nemerow integrated pollution index (NIPI) and potential ecological risk index (PERI). The results showed that Cd and Hg were the main pollutants in the study area. Health risk assessment results indicated that children were in higher non-carcinogenic and carcinogenic risks than adults with the carcinogenic metal of As. Ingestion was the main exposure pathway to non-carcinogenic and carcinogenic risk for both adults and children. Principal component analysis (PCA) indicated that Cr and Cu were mainly from parent materials, while Cd and As were mainly affected by agricultural activities. Pb and Zn were controlled by traffic activities, and the accumulations of Ni and Hg were associated with mining activities. This study would be valuable for preventing heavy metals inputs and safety in rice production of the Songhua river basin.
Keywords: spatial distribution; heavy metals; paddy soil; risk assessment; source identification; Songhua River Basin

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1 Introduction

Soil contaminations have become an important environmental concern in China with the changes of land use in the past decades (Liu et al., 2014). Anthropogenic activities, such as industrial and agricultural production,

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transportation, mining and smelting, have released plenty of toxic and harmful substances (e.g., heavy metals, polycyclic aromatic hydrocarbons and phthalate esters) into the soil (Wang et al., 2017). In particular, heavy metals contamination has become increasingly serious concern due to its potential threat to ecological environment, food safety, human health and agricultural sustainable development (Cui et al., 2004). Heavy metals in agricultural soils have increased mainly because of parent material, application of fertilizers and pesticides, wastewater irrigation, sewage sludge application and atmospheric deposition (Cai et al., 2009). Therefore, it is necessary to identify metal source and evaluate the contamination level and health risk. Natural and anthropogenic sources of soil heavy metals could be identified by employing multivariate analysis, including correlation analysis and principal component analysis (PCA) (Lu et al., 2012; Shan et al., 2013). Moreover, spatial analysis techniques could map distributions of heavy metals and identify the possible hotspots in soil. The contamination level and risks associated with heavy metals in agricultural soil have attracted much attention in recent years, with many methods being used for their evaluation (Qureshi et al., 2016; Huang et al., 2018). Among these methods, geo-accumulation index (I_{geo}), Nemerow integrated pollution index (NIPI) and potential ecological risk index (PERI) have been widely used (Chen et al., 2015; Ke et al., 2017). The I_{geo} is based on single metal, while the NIPI provides comprehensive information regarding the risks posed by the presence of multiple metals (Yang et al., 2011). A combination of these three methods could make a relatively precise assessment by considering the lithology, toxicity variation of heavy metals and comprehensive effect of multiple contaminants. The health risk assessment method has also been widely used to assess non-carcinogenic and carcinogenic risks of heavy metal to the public crowd (Man et al., 2010).

Rice is the most common crop in China with annual yield of 2.07×10^{11} kg, accounting for more than 34% of the total grain output (National Bureau of Statistics of China, 2014). Moreover, Jilin Province is one of the major rice-production bases in Northeast China with annual rice yield of 5.88×10^{9} kg, accounting for 17% of the total grain yield of Jilin Province (National Bureau of Statistics of China, 2014). The Songhua River is one of the most important rivers in Northeast China with the length and basin area of 958 km and 13368 km^2, respectively, where the paddy yield in Songhua River accounts for 3/4 of the total paddy farming area of Jilin province (Wang, 2016). Yongshuyu irrigation area is located in the right bank of Songhua River upstream basin and downstream of Jilin City, the heavy industrial city of Jilin Province. The irrigated water mainly comes from Songhua River which flows through industrial area of Jilin City, and received the contaminants from industrial discharges. Previous studies about agricultural soil pollution in Jilin Province were mainly focus on maize and vegetable soils (Sun et al., 2013; Liu et al., 2014), but the information about contamination level of paddy soils was limited (Zhu et al., 2011).

The purposes of this study were: 1) to investigate the occurrence and spatial distribution of heavy metals (Pb, Cr, Cu, Ni, Zn, Cd, Hg and As) in paddy soil; 2) to assess the pollution level, potential ecological risk and health risk of heavy metals; and 3) to identify the sources of heavy metals. This study would assist in evaluating heavy metal pollution status and conducting regular monitoring program in irrigation area of Songhua River. The results also could be used to designing future control programs and taking preventive actions to minimize human health risk.

2 Materials and Methods

2.1 Study area

Yongshuyu irrigation area is located in the upstream of the Songhua River basin with more than 70 years irrigating history and lies in 44°13′02″N to 44°28′38″N, 126°30′29″E to 126°38′17″E. The study area belongs to temperate continental monsoon climate, which characterized by long and cold winters and generally short and warm summers. The annual average temperature is 3.5℃ with the highest temperature 40℃ in summer, the lowest temperature –39.8℃ in winter. The annual precipitation averaged 600–750 mm with the average annual evaporation of 1421 mm and irrigation period evaporation of 581 mm. The paddy fields in this region received irrigation water for rice production year by year, and the main irrigation water is pumped from the Songhua River and delivered to the paddy fields through ditches.

2.2 Soil sampling and chemical analysis

A total of 20 soil samples were collected from Yongshuyu irrigation area in October 2014 (Fig. 1). Sampling design was based on the water flow direction according to the technical specification for soil environmental monitoring (State Environmental Protection Administration, 2004). Started from the canal head, representative sampling sites were selected which covered the whole irrigation area. Composite samples for each sampling site were consisted of 3–4 subsamples which were collected from the surrounding randomly. Approximately 1.0 kg of soil was taken for each site, and grass, leaves, and roots in soil samples were discarded after gentle shaking. All soil samples were air-dried, passed through a 2-mm nylon sieve, and stored in closed plastic bags until analysis.

Soil pH was measured (soil:water is 1.0:2.5 W/V) using a pH-meter (pH S-3B, Leici, Shanghai). Soil organic carbon (SOC) was determined by the Walkey-Black method (Nelson and Sommer, 1982). Soil total nitrogen (TN) was measured with the method of Kjeldah (Bradstreet, 1954). Air-dried soil samples were passed through a 100-mesh nylon sieve before analyzing concentrations of the eight heavy metals.

Soil samples were digested with the method of HNO_3-$HClO_4$-HF (MEPC, 1997) to extract the metals of Pb, Cr, Cu, Ni, Zn and Cd, and the concentrations of

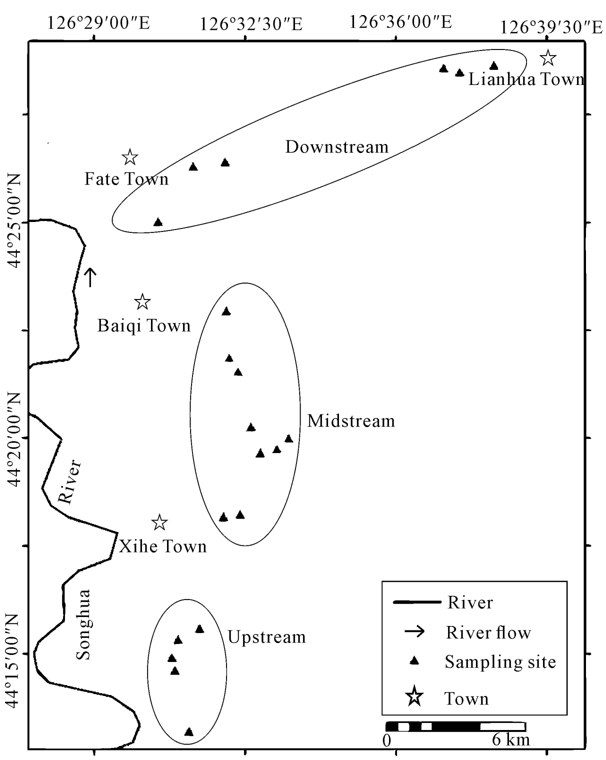

Fig. 1 Location of Yongshuyu irrigation area and distribution of the sampling sites

Pb, Cr, Cu, Ni and Zn in extracts were measured by Flame (air-acetylene) Atomic Absorption Spectrophotometer, FAAS (AA-6300C, Shimadzu, Japan), and concentrations of Cd were determined by Graphite Furnace Atomizer, GFA (AA-6300C, Shimadzu, Japan). Another soil samples were digested by water bath digestion with HNO_3 and HCl (Liu et al., 2015) to extract Hg and As. The concentrations of Hg and As were measured by non-dispersive atomic fluorescence photometer (PF6-2, PERSEE, China).

2.3 Pollution indices and potential ecological risk

Geo-accumulation index (I_{geo}) (Müller, 1969) and Nemerow integrated pollution index (NIPI) (Yu et al., 2004) were calculated for eight heavy metals to assess the pollution degree. Hakanson risk indices were used to estimate the level of potential ecological risk of heavy metals (Hakanson, 1980).

(1) The calculation of I_{geo}

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \tag{1}$$

where n is a heavy metal element; C_n is the heavy metal (n) concentration; B_n is the heavy metal geochemical background value of Jilin Province (Meng and Li, 1995). The pollution degree is categorized as follows: $I_{geo} \le 0$, none pollution; $0 < I_{geo} \le 1$, light-moderate; $1 < I_{geo} \le 2$, moderate; $2 < I_{geo} \le 3$, moderate-heavy; $3 < I_{geo} \le 4$, heavy; $4 < I_{geo} \le 5$, heavy-extremely; $I_{geo} > 5$, extremely.

(2) The calculation of NIPI

$$NIPI = \sqrt{\frac{PI^2_{i\max} + PI^2_{i\text{ave}}}{2}} \tag{2}$$

$$PI = C_n / T_n \tag{3}$$

where PI is the pollution index of each heavy metal; i is the number of samples; T_n is the corresponding reference concentration (MEPC and SBTS, 1995); $PI_{i\text{ave}}$ and $PI_{i\max}$ are the average value and the maximum value of all PI, respectively. The $NIPI$ degree is categorized as follows: $NIPI \le 0.7$, safe; $0.7 < NIPI \le 1$, precaution; $1 < NIPI \le 2$, slight pollution; $2 < NIPI \le 3$, moderate pollution; $NIPI > 3$, high pollution.

(3) The calculation of potential ecological risk index (PERI)

$$E_r = T_r \times \frac{C_s}{C_{\text{ref}}} \tag{4}$$

$$RI = \sum_{i=1}^{n} E_r = \sum_{i=1}^{n} T_r \times \frac{C_s}{C_{\text{ref}}} \quad (5)$$

where E_r is the potential risk of each heavy metal; T_r is the metal toxic factor (Ke et al., 2017); C_s is the heavy metal concentration; C_{ref} is the concentration of the same heavy metal in the reference soil; *RI* is the comprehensive potential ecological risk index; *n* is the number of heavy metals. Since the number of pollutants considered in our study was different from that of Hakanson (1980), the risk degree and evaluation classification were adjusted (Vu et al., 2017). The PERI of heavy metals is categorized and shown in Table 1.

2.4 Health risk assessment

The hazard quotient (HQ) and cancer risk (CR) are used to quantitatively explain non-carcinogenic and carcinogenic risks of exposure to heavy metals, respectively, where three exposure pathways are considered: direct ingestion, dermal absorption and inhalation (Tepanosyan et al., 2017). According to the Exposure Factors Handbook (US. EPA, 1997), the average daily dose (ADD) (mg/(kg·d)) of a pollutant via ingestion, dermal contact and inhalation as exposure pathways can be estimated using Eqs. (6)–(8):

$$ADD_{\text{ingest}} = \frac{C_{\text{soil}} \times IngR \times EF \times ED}{BW \times AT} \times CF \quad (6)$$

where C_{soil} is heavy metal concentration (mg/kg); *IngR* is the ingestion rate (mg/d); *EF* is the exposure frequency (d/yr); *ED* is the exposure duration (yr); *BW* is the average body weight (kg); *AT* is the time period over which the dose is averaged (d); *CF* is the conversion factor (1×10^{-6} kg/mg).

$$ADD_{\text{dermal}} = \frac{C_{\text{soil}} \times SA \times AF_{\text{soil}} \times ABS \times EF \times ED}{BW \times AT} \times CF \quad (7)$$

Table 1 Indices and grades of potential ecological risk factor (E_r) and potential risk index (*RI*)

E_r	*RI*	Risk level
≤40	<110	Low
40–79	110≤ RI<200	Moderate
80–159	200≤ RI<400	Considerable
160–320	≥400	High
≥320	–	Very high

where *SA* is the surface area of the skin that contacts the soil (cm^2); *AF* is the skin adherence factor (mg/cm^2); *ABS* is the dermal absorption factor.

$$ADD_{\text{inhale}} = \frac{C_{\text{soil}} \times InhR \times EF \times ED}{PEF \times BW \times AT} \quad (8)$$

where *InhR* is the Inhalation rate (m^3/d); *PEF* is the particle emission factor (1.36×10^9 m^3/kg).

The potential non-carcinogenic and carcinogenic risks for individual metals were calculated using the following equations (Eqs. (9)–(11)) (US. EPA, 1989):

$$HQ = \frac{ADD}{RfD} \quad (9)$$

$$HI = \sum HQ_i \quad (10)$$

$$CR = \sum ADD_i \times SF_i \quad (11)$$

where *RfD* is the reference dose (mg/(kg·d)); H*I* is the sum of *HQ*; *SF* is the slope factor (per (mg/(kg·d)). *HI* values > 1 indicates there is a chance that non-carcinogenic effects may occur, while values < 1 indicates lower or no risk of non-carcinogenic effects (US. EPA, 2001); $CR > 1 \times 10^{-4}$ is viewed as unacceptable, while $CR < 1 \times 10^{-6}$ is not considered to pose significant health effects, and $1 \times 10^{-6} < CR < 1 \times 10^{-4}$ is regarded as a tolerable degree (Chen et al., 2015; Li et al., 2017). The detailed information of the health risk assessment parameters is provided in Table 2.

2.5 Principal component analysis

Principal component analysis (PCA) was carried out to cluster metals that behaved similarly to identify the potential sources (Pan et al., 2016). Varimax rotation was applied as orthogonal rotation to minimize the number of variables with a high loading on each component and facilitate the interpretation of results. Heavy metals with < 0.5 measurements of the proportion of variance explained by the extracted components (communality values) were excluded from PCA.

2.6 Quality assurance/quality control (QA/QC) and statistical analyses

The standard reference material (GBW 07405 [GSS-5]) obtained from the Center of National Standard Reference Material of China was used in the digestion and determination as part of the quality assurance (QA) protocol. Reagent blanks and analytical duplicates were

Table 2 Parameters of human health risk assessment

Parameter	Symbol	Unit	Adults	Children	Reference
Ingestion rate of soil	IngR	mg/d	100	200	(US. EPA, 1997)
Exposure frequency	EF	d/yr	350	350	(Man et al., 2010)
Exposure duration	ED	yr	30	6	(Man et al., 2010)
Average body weight	BW	kg	60	15	(Man et al., 2010)
Surface area of the skin that contacts soil	SA	cm^2	3300	2800	(US. EPA, 1997)
Average time	AT	d	Non-carcinogens: ED × 365 Carcinogens: 70 × 365		(US. EPA, 1989)
Conversion factor	CF	kg/mg	1×10^{-6}		(Man et al., 2010)
Skin adherence factor for soil	AF_{soil}	mg/cm^2	0.2		(US. EPA, 1997)
Dermal absorption factor	ABS	–	As: 0.03 Pb, Cr, Cu, Ni, Zn, Cd: 0.001		(US. EPA, 2011)
Inhalation rate	InhR	m^3/d	20		(US. EPA, 1997)
Particle emission factor	PEF	–	$1.36 \times 10^9\ m^3/kg$		(US. EPA, 2001)
Reference dose	RfD	mg/(kg·d)	Ingestion RfD: Cd:0.001 Cr:0.003 As:0.003 Pb:0.0035 Cu:0.04 Zn:0.3 Ni:0.02 Hg:0.0003 Dermal RfD: Cd:1.00E-05 Cr:6.00E-05 As:1.23E-04 Pb:5.25E-04 Cu:1.20E-02 Zn:6.00E-02 Ni:5.40E-03 Hg:2.10E-05 Inhalation RfD: Cd:1.00E-03 Cr:2.86E-05 As:1.23E-04 Pb:3.50E-03 Cu:4.00E-02 Zn:0.3 Ni:2.06E-02 Hg:8.57E-05		(Li et al., 2014)
Slope factor	SF	per mg/(kg·d)	Ingestion SF: As:1.50 Dermal SF: As:3.66 Inhalation: Ni:0.84 Cr:42.0 Cd:6.30 As:15.1		(Li et al., 2014)

used for ensuring the accuracy and precision of analysis. Glass wares were soaked overnight with HNO_3 (10% v/v) and rinsed thoroughly with deionized water. The recovery ratios for the eight observed metals were between 90% and 110%. Statistical analysis in this study was performed using SPSS 16.0 and Excel 2016. Spatial analysis by GIS was also used to graphically and digitally present the distribution of the studied metals. Heavy metal distribution maps were created using ArcGIS 9.0.

3 Results and Discussion

3.1 Descriptive statistics of heavy metals concentration in paddy soil

The main statistical characteristics of metal concentrations and soil properties were presented in Table 3. Soil pH ranged from 5.17 to 6.17 with a mean value of 5.55. All the soils were slightly acidic which was partly due to the use of high amounts of chemical fertilizers (especially N fertilizer) with the efficiencies of only 30%–50% in China (Guo et al., 2010). SOC was in the range of 11.1 to 20.6 g/kg with a mean value of 15.0 g/kg. SOC could play a significant role in the preservation of heavy metals in soils due to its strong adsorption (Micó et al., 2006). On the other hand, the pH value could influence the cation mobility and regulate the solubility of heavy metals in soil (Kashem and Singh, 2001), and most of the metals tend to be available in acid pH, with the exception of Cd (Martín et al., 2006). Therefore, further researches were required to assess the potentially available species (e.g., extractable fraction), mobility, phytoavailability, and bioaccessibility of heavy metals to determine the probability of the metals transferring from the soil to other ecosystems, such as the underground water or crops.

The concentrations of heavy metals were in the range of 28.80–45.50 mg/kg for Pb, 68.00–97.70 mg/kg for Cr, 10.30–24.80 mg/kg for Cu, 7.95–47.00 mg/kg for Ni, 60.50–120.00 mg/kg for Zn, 0.06–0.76 mg/kg for Cd, 0.11–0.38 mg/kg for Hg and 4.13–13.30 mg/kg for As, with the average concentrations of 34.60, 82.80, 17.30, 21.20, 88.60, 0.18, 0.22 and 8.77 mg/kg, respectively. The percentage of exceeding background values were 100% for Pb, Hg and Cr, 95% for Zn, 90% for As, 85% for Cd, 70% for Cu and 40% for Ni, respectively. The results indicated that anthropic inputs such as long-term agricultural practices and industry activities

Table 3 Descriptive statistics of soil properties and heavy metals concentrations (n = 20)

Heavy metals	Min	Max	Median	Mean	S.D[a]	CV (%)[b]	BC (mg/kg)[c]	GBI	GBII
Pb (mg/kg)	28.65	45.47	33.46	34.57	4.67	13.50	22.16	35.00	250.00
Cr (mg/kg)	68.01	97.73	84.79	82.83	9.51	11.48	48.29	90.00	250.00
Cu (mg/kg)	10.27	24.79	17.70	17.25	4.09	23.68	15.10	35.00	50.00
Ni (mg/kg)	7.95	46.97	16.95	21.17	11.97	56.52	20.07	40.00	40.00
Zn (mg/kg)	60.52	119.85	82.73	88.57	17.90	20.21	61.79	100.00	200.00
Cd (mg/kg)	0.06	0.76	0.15	0.18	0.15	82.86	0.10	0.20	0.30
Hg (mg/kg)	0.11	0.38	0.24	0.22	0.07	33.49	0.04	0.15	0.30
As (mg/kg)	4.13	13.41	8.60	8.77	2.47	28.18	5.93	15.00	30.00
pH	5.17	6.17	5.53	5.55	0.28	5.02			
SOC (g/kg)	11.06	20.55	15.29	14.96	2.70	18.11			

Notes: a: Standard deviation. b: Coefficients of variation. c: Background concentrations of Jilin topsoil. GBI: Grade I value of the Environmental Quality Standard for Soils of China (MEPC and SBTS, 1995). GBII: Grade II value of the Environmental Quality Standard for Soils of China (MEPC and SBTS, 1995). SOC: Soil organic carbon

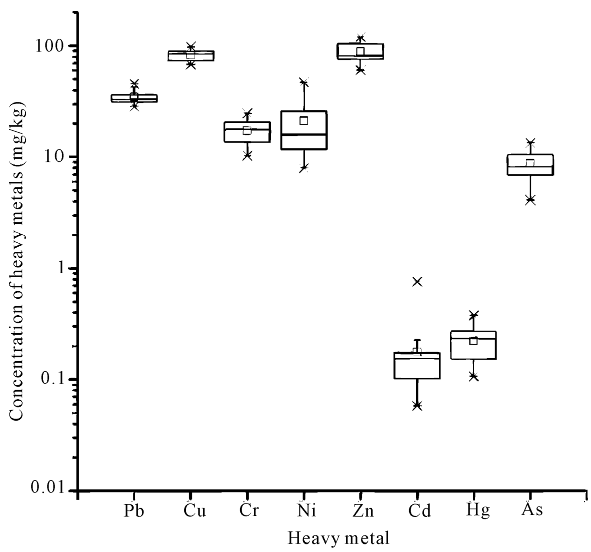

Fig. 2 Box-plots of heavy metals in paddy soil

caused a significant enrichment of heavy metals in agricultural soils (Sun et al., 2013). The Chinese Environmental Quality Standard for Soils regulated the concentration limit of heavy metal for protection of agricultural products and human health (MEPC and SBTS, 1995). In this article, heavy metal concentrations did not exceed the concentration limits with the exception of Cd in one sample, Ni and Hg in two samples. This indicated that it was still safe and suitable for agricultural production in this study area.

Heavy metal concentrations of different type soils in and out Jilin Province were summarized in Table 4. Compared with Qianguo irrigation area which was located in the downstream of the study area, the heavy metal concentrations were slightly higher except for Pb, Cu and Ni. Compared with other type soils in Jilin Province, the concentrations of eight heavy metals were higher than that of grassland soils in Baicheng and Songyuan regions, and Pb, Cr, Zn and Cd concentrations were higher than those of vegetable soils in Changchun City, Dehui County and Nong'an County. Pb, Cr and Hg concentrations in study soil were significantly higher than those of agricultural soil in Beijing, Shangdong and Changshu, while Cu and Ni were in lower concentrations and there were not much difference among Zn, Cd and As. Compared with the urban soil in Shenyang, Anshan and Tanggu, heavy metal concentrations in Yongshuyu irrigation were much lower except for Cr, which might be owing to there were obvious heavy metal emission sources in these three cities. In general, the heavy metals concentrations in Yongshuyu irrigation were lower than those in urban soils but relatively high among agricultural soils.

3.2 Spatial distribution of heavy metals in irrigation area

Spatial distributions of heavy metals in Yongshuyu irrigation area were shown in Fig. 3. The hotspots of As and Cd were concentrated in the up-midstream of the irrigation area. According to Jilin Statistical Yearbook (2016), large quantities of phosphatic fertilizers and pesticides were used in rice farming processes and had been proved to be a significant source of some heavy metals especially for Cd and As (Bhattacharya et al., 2007; Sun et al., 2013). Cr and Cu showed similar spatial distributions with hotspots distributed uniformly in the irrigation area, which the mean concentrations were close to their background concentrations with relatively low coefficient of variation, reflecting slightly effects from anthropogenic activities. Variability of Ni concentration was observed from upstream to downstream with high Ni concentrations in the downstream, where Ni quarries with different scales distributed. The hotspots with high concentration of Hg were mostly located in the upstream and downstream which were mainly due to the irrigation

Table 4 Comparison of average concentration of heavy metals in soils reported in literature (mg/kg)

Region	Province	Soil types	Pb	Cr	Cu	Ni	Zn	Cd	Hg	As	References
Qianguo irrigation area	Songyuan, Jilin Province	Paddy soil	47.00	na	20.60	27.20	68.00	0.16	0.07	6.27	(Zhu et al., 2011)
Changchun	Jilin Province	Vegetable soil	20.80	61.40	20.90	28.20	71.40	0.14	na	na	
Dehui County	Changchun, Jilin Province	Vegetable soil	24.60	72.60	20.00	35.70	76.30	0.09	na	na	(Liu et al., 2014)
Nong'an County	Changchun, Jilin Province	Vegetable soil	31.70	55.20	22.70	25.80	84.00	0.13	na	na	
Baicheng-Songyuan	Jilin Province	Grassland soil	18.30	35.00	16.70	15.20	35.00	0.07	0.01	7.20	(Chai et al., 2015)
Shenyang	Liaoning Province	Urban soil	118.00	67.90	92.50	na	235.00	1.10	0.39	22.70	(Li et al., 2013)
Anshan	Liaoning Province	Urban soil	45.10	69.90	52.30	33.50	213.00	0.86	na	na	(Xiao et al., 2015)
Beijing		Agricultural soil	20.40	na	22.40	na	69.80	0.14	0.07	7.85	(Lu et al., 2012)
Tanggu	Tianjin	Urban soil	45.00	51.00	33.00	39.00	148.00	0.18	0.43	11.00	(Zhao et al., 2014)
Shandong Province	Shandong Province	Agricultural soil	16.20	41.80	29.30	28.00	82.30	0.15	0.09	9.02	(Liu et al., 2011)
Changshu	Jiangshu Province	Agricultural soil	26.30	na	31.00	29.50	81.90	0.17	na	na	(Ran et al., 2016)
This study area		Paddy soil	34.60	82.80	17.30	21.20	88.60	0.18	0.22	8.77	

Note: na: not available

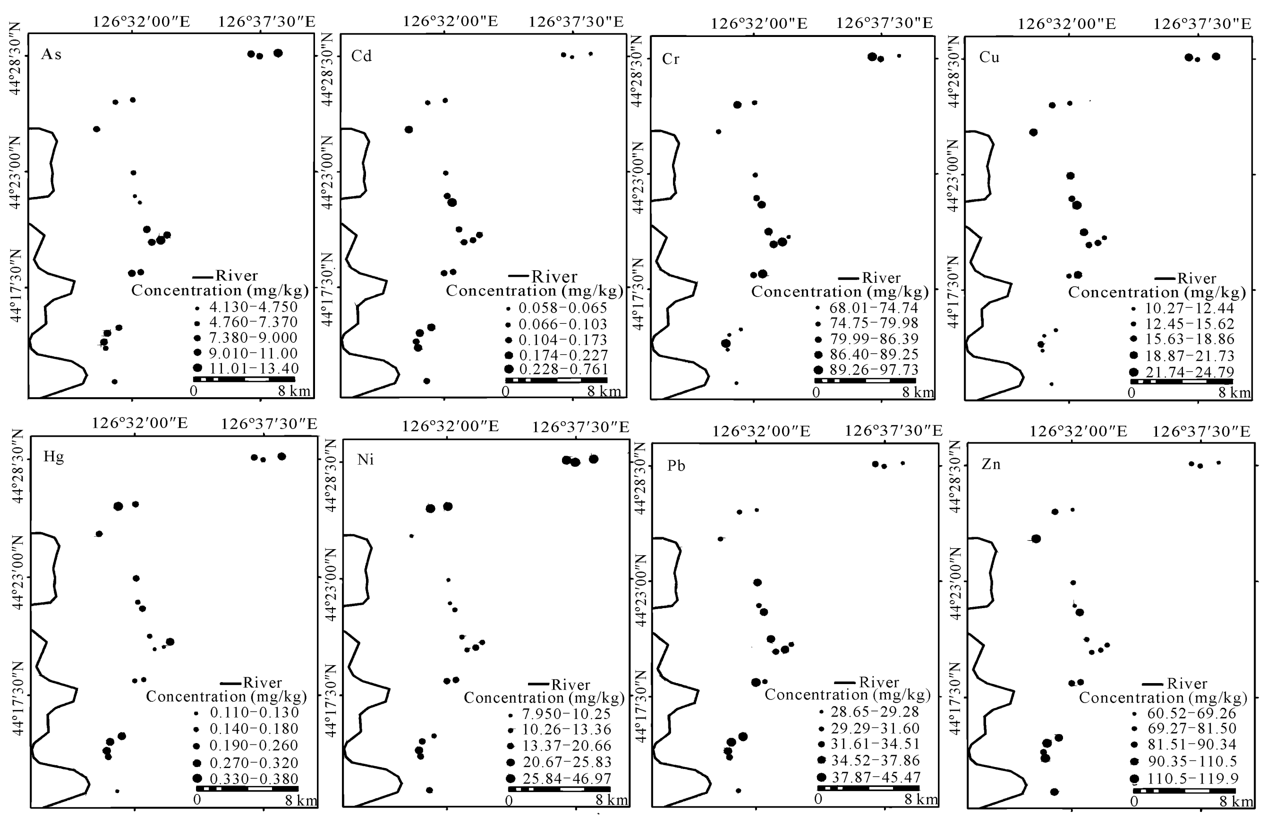

Fig. 3 Spatial distribution of heavy metals in soils of Yongshuyu irrigation area

water and coal mining emissions (Pan et al., 2016). The spatial variations of Pb and Zn concentrations were consistent in certain area, and the hotspots were mainly distributed along highway sides (National Highway 202) where high traffic density was identified.

3.3 Pollution assessment of heavy metals in irrigation area

The I_{geo} and NIPI of heavy metals were presented in Table 5. The mean values of I_{geo} were in a decreasing order of Hg (1.99) > Cr (0.18) > Cd (0.07) > Pb (0.05) > As (–0.08) > Zn (–0.09) > Cu (–0.43) > Ni (–0.71). The mean values of Cu, Ni, Zn and As showed none contamination, while those of Pb, Cr and Cd light-moderate contamination, and that of Hg moderate contamination. The NIPI values were ranged from 0.40 to 1.85 with mean value of 0.70, revealing that the study area was in safe or precautious degree except for one site of slight pollution degree.

3.4 Potential ecological risk of heavy metals in irrigation area

The E_r and RI values of heavy metals were calculated in Table 6. The RI values were all above 110 for the study area, indicating that PERI of heavy metals were all in moderate or more serious degree. All sample sites were found in the considerable potential ecological risk with 25% in the high degree. High RI values (RI > 110) were observed to be uniform with the hotspots of Hg E_r value, indicating that Hg was the main contributor to heavy metals RI, which accounted for 59.1%–79.1% among the eight heavy metals for the RI. The results highlighted that Hg posed higher risk to the ecosystem. The high ecological risk of Hg might be owe to its anthropogenic activities, such as coal combustion, mining operation and vehicular emission over several decades and higher toxic factor. Thus, relevant measures should be taken to avoid further soil pollution and to ensure the ecological safety.

Table 5 Grading statistic of soil heavy metals in paddy soils

	Heavy metals	Min	Max	Median	Mean	Pollution level
I_{geo}	Pb	–0.21	0.45	0.01	0.05	Light-moderate
	Cr	–0.09	0.43	0.23	0.18	Ligh-moderate
	Cu	–1.14	0.13	–0.36	–0.43	None
	Ni	–1.92	0.64	–0.83	–0.71	None
	Zn	–0.61	0.37	–0.16	–0.09	None
	Cd	–1.30	2.42	0.11	0.07	Light-moderate
	Hg	1.03	2.85	2.18	1.99	Moderate
	As	–1.11	0.59	–0.05	–0.08	None
NIPI		0.40	1.85	0.69	0.70	Precaution

Notes: I_{geo}: geo-accumulation index. NIPI: Nemerow integrated pollution index

Table 6 Potential ecological risk factor (E_r) and potential risk index (RI) of heavy metals

	Heavy metals	Min	Max	Median	Mean	Risk level
E_r	Pb	6.46	10.30	7.55	7.80	Low
	Cr	2.82	4.05	3.51	3.43	Low
	Cu	3.40	8.21	5.86	5.71	Low
	Ni	1.98	11.70	4.22	5.27	Low
	Zn	0.98	1.94	1.34	1.43	Low
	Cd	18.30	240.00	48.50	55.80	Moderate
	Hg	123.00	434.00	272.00	253.00	High
	As	6.96	22.60	14.50	14.80	Low
RI		208	549	347	358	Considerable

3.5 Health risk assessment of heavy metals in irrigation area

The results of non-carcinogenic and carcinogenic health risks posed by eight heavy metals in paddy soils for adults and children via different pathways were shown in Table 7. Missing values were due to a lack of corresponding RfD or SF values. The total HI values were 0.15 and 2.00 for adults and children, respectively. The total HI value for children was greater than 1, indicating that children might experience non-carcinogenic effects. The HQ values for children were in the decreasing order: Cr > As > Pb > Cd > Hg > Ni > Zn > Cu. Among these elements, HQ value of Cr exceeded 1, accounting for 88.58% of the total HI. Children were in higher non-carcinogenic risks than adults through three pathways, which indicated that children were more susceptible for the heavy metal affection to the body. This might be due to the behavioral and physiological characteristics of children, including hand-to-mouth activities in soil and higher respiration rates per unit body weight. The contributions of the ingestion pathway were the highest (99.34% for children and 74.05% for adults), followed by dermal contact and inhalation, indicating that ingestion was the primary pathway that harmful to human health. These results were also consistent with other earlier studies (Jiang et al., 2017; Li et al., 2017).

Since Pb, Cu, Zn and Hg were not in the carcinogenic category (US.EPA, 1997). As was estimated in all three pathways for the carcinogenic health risks, while Cr, Ni and Cd were assessed only in inhalation pathway. The total CR values for adults and children were 3.202×10^{-5} and 2.060×10^{-4}, respectively (Table 6). The carcinogenic risk for children was higher than the maximum tolerable value (1×10^{-4}), while the carcinogenic risk for adults was in acceptable range (1×10^{-6} to 1×10^{-4}). The CR values of Ni and Cd for both adults and children, and Cr for adults were below the negligible risk level of 1×10^{-6}, indicating that no significant health effects. The CR values of As for adults and Cr for children stood in the range of acceptable risk (1×10^{-6} to 1×10^{-4}), whereas the CR values of As for children was 2.028 times of the threshold for the carcinogenic risk. Ingestion accounted for 65.67% and 81.65% of the total CR for adults and children, respectively, which were much higher than the other two pathways, indicating that ingestion was the primary heavy metals exposure pathway to both adult and children.

3.6 Source identification of heavy metals in paddy soil

Correlation coefficients between soil properties and heavy metals were presented in Table 8. The pH values showed a low relationship with all the elements analyzed. However, the moderate positive correlation was found between SOC and Cu (r = 0.55, P < 0.05), TN and Ni (r = 0.46, P < 0.05). Cr and Cu, Cd and TP were found in significant positive correlation (r = 0.68, P < 0.01), which indicated that they might be from similar sources (Micó et al., 2006). Cd and As were in moderate negative correlation (r = –0.46, P < 0.05).

Table 7 Estimations of non-carcinogenic (Hazard Quotient, HQ) and carcinogenic health risks (Cancer Risk, CR) from heavy metals in soil

Risk	Heavy metal	Adults				Children			
		Ingestion	Dermal	Inhalation	Total pathways	Ingestion	Dermal	Inhalation	Total pathways
Hazard Quotient	Pb	1.579E-02	6.946E-04	2.272E-06	1.648E-02	8.420E-01	2.358E-03	9.086E-06	8.444E-01
	Cr	4.413E-02	1.456E-02	6.660E-04	5.936E-02	1.765E+01	4.942E-02	2.664E-03	1.770E+01
	Cu	6.893E-04	1.516E-05	9.918E-08	7.046E-04	1.838E-02	5.147E-05	3.967E-07	1.843E-02
	Ni	1.692E-03	4.135E-05	2.363E-07	1.733E-03	5.012E-02	1.403E-04	9.453E-07	5.026E-02
	Zn	4.718E-04	1.557E-05	6.789E-08	4.875E-04	1.887E-02	5.284E-05	2.716E-07	1.893E-02
	Cd	2.829E-04	1.867E-04	4.070E-08	4.696E-04	2.263E-01	6.336E-04	1.628E-07	2.269E-01
	Hg	1.180E-03	1.113E-04	5.944E-07	1.292E-03	1.349E-01	3.776E-04	2.378E-06	1.352E-01
	As	4.673E-02	2.257E-02	1.640E-05	6.931E-02	9.117E-01	7.658E-02	6.559E-05	9.884E-01
	Total	1.110E-01	3.819E-02	6.857E-04	1.498E-01	1.985E+01	1.296E-01	2.743E-03	1.999E+01
Cancer Risk	Cr	–	–	8.000E-07	8.000E-07	–	–	3.200E-06	3.200E-06
	Ni	–	–	4.089E-09	4.089E-09	–	–	1.636E-08	1.636E-08
	Cd	–	–	2.564E-10	2.564E-10	–	–	1.026E-09	1.026E-09
	As	2.103E-05	1.016E-05	3.046E-08	3.122E-05	1.682E-04	3.448E-05	1.218E-07	2.028E-04
	Total	2.103E-05	1.016E-05	8.348E-07	3.202E-05	1.682E-04	3.448E-05	3.339E-06	2.060E-04

Table 8 Pearson correlations matrix for the heavy metal concentrations and soil properties

Heavy metal	Pb	Cr	Cu	Ni	Zn	Cd	Hg	As	SOC	pH	TN	TP
Pb	1	0.00	−0.20	−0.34	0.36	0.23	0.06	0.25	−0.39	0.08	−0.20	0.14
Cr		1	**0.68****	0.21	−0.35	0.03	−0.24	0.17	0.24	0.16	0.14	0.14
Cu			1	0.02	−0.27	0.27	−0.04	0.00	**0.55***	0.34	0.30	0.41
Ni				1	−0.36	−0.37	0.35	0.19	0.28	0.02	**0.46***	−0.13
Zn					1	0.44	0.18	-0.17	−0.28	0.09	−0.16	0.36
Cd						1	0.06	**−0.46***	−0.02	0.40	0.09	**0.93****
Hg							1	−0.09	0.02	0.08	0.06	0.11
As								1	0.03	0.10	0.09	−0.40

Notes: SOC: soil organic carbon.TN: total nitrogen. TP: total phosphorus. **:Correlation is significant at the 0.01 level (2-tailed). *:Correlation is significant at the 0.05 level (2-tailed).

Varimax rotation results of the four components were shown in Table 9. PC1, PC2, PC3 and PC4 could explain the 82.9% of the total variance. PC1 explained 23.3% of the total variance and presented high positive loading values (> 0.7) for Cr and Cu, which suggested that Cr and Cu might have similar source. Although the mean concentrations of Cr for all sampling sites exceeded the background value, the concentrations in most areas were still under control, and the low coefficient of variation (C.V. = 11.5%) also indicated that Cr might be mainly controlled by soil characteristics. The mean value of Cu was close to the background value and in moderate positive correlation with SOC, which indicated that Cu was mainly affected by parent materials. Therefore, it could be concluded that Cr and Cu might mainly come from nature source.

PC2 explained 22.4% of the total variance and showed strong negative loadings for Cd and strong positive loading for As, which indicated that the two elements might come from different sources. Cd was usually considered as marker element of agricultural activities which included the use of pesticides and chemical fertilizers. The significant positive correlation between Cd and TP reflected that the source of Cd was mainly from phosphoric fertilizers. Inorganic As compounds such as calcium arsenate, lead arsenate, sodium arsenate and many others were used largely as pesticides or herbicide (Bhattacharya et al., 2007), thus, they might be the important sources of As. These suggested that Cd and As might mainly come from agricultural practices.

PC3 explained 20.8% of the total variance for Pb and Zn. Over the past 50 years, vehicle emissions had been regarded as the main source of Pb in agricultural soil, which had been verified by many related studies (Sun et al., 2013; Liu et al., 2015). The wear and tear of vulcanized vehicle tires and corrosion of galvanized automobile parts were the primary sources of Zn (Lu et al., 2010). Thus, Pb and Zn might come from traffic activities.

PC4 explained 16.3% of the total variance for Ni and Hg. Both anthropogenic sources and soil parent materials might release Ni into the environment, and relevant studies also showed that the long-term human activities which affected the accumulation of Ni were mining activities (Luo et al., 2010). A large part of Hg emissions were mainly from the small-scale mining process (Streets et al., 2005), and more than 1450 km^2 of mining land located in Shulan city near the downstream of the irrigation area (Shi, 2013). Therefore, Ni and Hg would be related to mining operations.

Table 9 Eigenvalues, Cumulative percentage and matrix of principal component analysis (PCA)

Heavy metals	Component			
	PC1	PC2	PC3	PC4
Pb	−0.02	0.15	**0.90**	−0.05
Cr	**0.90**	0.17	−0.04	−0.08
Cu	**0.90**	−0.19	−0.11	0.02
Ni	0.14	0.38	−0.44	**0.67**
Zn	−0.35	−0.44	**0.62**	0.08
Cd	0.25	**−0.79**	0.40	−0.02
Hg	−0.12	−0.14	0.13	**0.92**
As	0.13	**0.86**	0.29	0.00
Eigenvalue	1.86	1.79	1.67	1.31
Total variance (%)	23.30	22.40	20.80	16.30
Cumulative variance (%)	23.30	45.70	66.60	82.90

Note: Items of high loadings were bold in each principal component

4 Conclusions

This study examined the concentrations, pollution level, spatial distribution, health risk and possible sources of eight heavy metals in paddy soils of Yongshuyu irrigation area, Northeast China. Although a slightly higher than their corresponding background values of Jilin Province topsoil, heavy metal concentrations did not exceed the guideline values of Chinese Environmental Quality Standard with the exception of Cd in one sample, Ni and Hg in two samples, indicating certain accumulation of these metals in this area. Among all the analyzed metals, Cr and Cu mainly come from the parent materials, and the spatial distribution showed a non-point source contamination, suggesting no significant anthropic input of Cr and Cu in the study area. Human activities, such as agricultural production, vehicle emissions and mining activities, were the main sources of Cd, As, Pb, Zn, Ni and Hg. The hot-spots of Cd and As were mainly distributed in the up-midstream where large amount of phosphatic fertilizers and pesticides applied, while the hot-spot of Ni was in the downstream where Ni quarries concentrated. Irrigation water and coal mining emission were the main factors for the hot-spots distribution of Hg in the upstream and downstream, respectively. The hot-spots of Pb and Zn were mainly distributed along the highway side. Primary contaminants in paddy soil were Pb, Cr, Cd and Hg. Nemerow integrated pollution index further estimated the composite risk of eight metals which indicated that half of the study areas were above precautions degree. Cd and Hg were the two most important factors affecting the soil environment. Consequently, Cd and Hg were the main contributors for the soil contamination in Yongshuyu irrigation area which were associated with anthropogenic activities. The results of health risk assessments suggested that children in study area might suffer higher non-carcinogenic and carcinogenic risk compared with adults. Cr was the main factor for children's non-carcinogenic risk, and the carcinogenic risk was primary associated with As. Ingestion was the primary exposure pathway for non-carcinogenic and carcinogenic risk. Therefore, further study is needed to explain the reasons for the higher health risk caused mainly by As and Cr in the study areas. This study will provide a basis for effectively targeting policies to reduce metal inputs and to protect paddy soils from long-term heavy metal accumulation.

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