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Heavy metal concentrations in water and soil along the Hun River, Liaoning, China

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Abstract Water and soil samples were collected along the Hun River to study the concentrations of Cr, Cu and Zn during the dry season, medium season and wet season in 2013. The concentrations of Cr, Cu, and Zn in Hun River were 0.0010 to 0.1298, 0.0057 to 0.1533 and 0.0162 to 0.5004 mg/L, respectively. The concentrations of Cr, Cu, and Zn in soil from around the Dahuofang reservoir were 0.0033 to 0.2149, 0.0054 to 0.2218 and 0.0135 to 0.3544 mg/g, respectively. The results indicated that the concentrations of Cr, Cu and Zn in water from the Hun River and soil from around the Dahuofang reservoir were significantly different at different sample stations and seasons. The pollution indexes of Cr, Cu and Zn in water and soil along the Hun River were calculated using principal component analysis in order to enact future measures against heavy metal pollution. According to the pollution characteristics of heavy metals along the Hun River, a treatment strategy was formulated to provide a scientific basis for the prevention and control of heavy metal pollution along the Hun River.

Keywords Heavy metals · Pollution index · Hun River · Dahuofang reservoir

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In recent years, there has been growing international concern about heavy metal pollution, particularly with regard to water and soil pollution (Akbulut and Tuncer 2011; Diagomanolina et al. 2004; Fekri and Kaveh 2013; Qian et al. 2005; Wang et al. 2004). Since heavy metals are easily absorbed into the food chain through bioaccumulation processes, aquatic life and humans are threatened by the accumulation of heavy metals in water and soil (Lv et al. 2011; Arunakumara et al. 2013).

The Hun River is the second largest river in the Liaoning province of China, and the Dahuofang reservoir is located in the upstream of the Hun River. The Hun River originates from Gunmaling mountain near the Qingyuan city and has a total length of 415 km and drainage area of 25,000 km^2. The Hun River runs through many industrial cities in the northeastern part of China, such as Qingyuan city, Fushun city, and Shenyang city. According to the Environmental Quality Standards for Surface Water of China (GB3838-2002), it has been reported that the water quality of the Hun River exceeds the Category IV standards of the China surface water environmental quality standard, and the soil along the Hun River has been found to be polluted by heavy metals. Heavy metals along the Hun River may come from natural sources, anthropogenic sources, mining, fertilizer and industrial and municipal sewage. Hun River provides water for industry and agriculture and is the source of drinking water for seven cities, such as Fushun city, Shenyang city, and Anshan city; therefore, the presence of heavy metals along the Hun River poses a risk to aquatic life and humans. Hu et al. assessed the water quality of the Hun River in 2010 using a single-factor water quality identification index and obtained the comprehensive water quality grade for monitored sections along the Hun River from 2001 to 2010 (Hu and Su 2011). Ma et al. reported the statistical analysis of heavy metal contents in soils

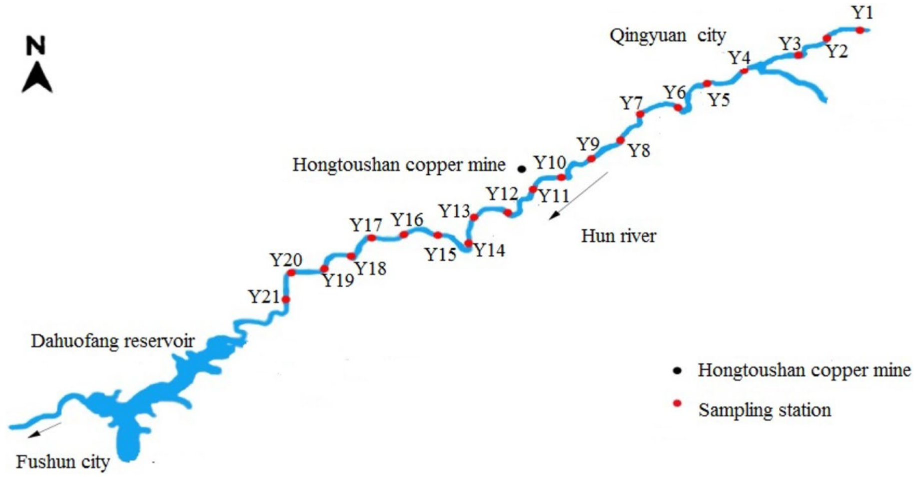

Fig. 1 Water sampling stations in the Hun River

from Zhangyi town and obtained the spatial distribution of heavy metal contents (Ma et al. 2014b). According to the measured data concerning heavy metals in the research area, Cr, Cu and Zn showed significant pollution and posed a considerable ecological risk at some of the sample stations. The objective of this study is to evaluate heavy metal (Cr, Cu and Zn) pollution in water from the upstream of the Hun River and in soil from around the Dahuofang reservoir. This report reveals the relationships between the degree of heavy metal pollution in the Hun River basin and its influencing factors, such as mining area, season and so on. The research reveals the characteristics of heavy metal pollution and provides a theoretical basis for the treatment of heavy metal pollution along the Hun River. For example, we should take different measures to deal with heavy metal pollution according to different pollution characteristics. It is clear that this study has obvious regional environmental protection and governance significance. In this study, the concentrations of Cr, Cu and Zn in water and soil along the Hun River were determined at different sampling stations during the dry season, medium season and wet season in 2013. Furthermore, we obtained the pollution indexes of Cr, Cu and Zn along the Hun River to assess the impact of heavy metal pollutants on the Hun River basin. The results provide a theoretical basis to ensure that the water and soil along the Hun River meet the natural environment standard for the health of aquatic life and humans.

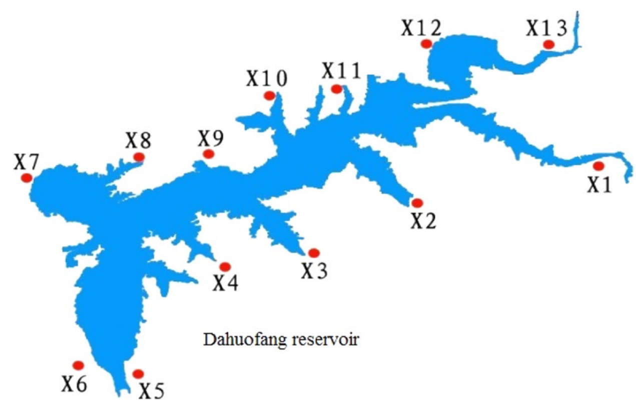

Fig. 2 Soil sampling stations around the Dahuofang reservoir

Table 1 Type of land around the Dahuofang reservoir

*X*1–*X*4	*X*5–*X*7	*X*8–*X*10	*X*11–*X*13
Flood land	Forest land	Uncultivated land	Farm land

Materials and Methods

The geographic coordinates of the research area are 41°30′10″–42°15′32″N, 120°20′42″–124°55′58″E. According to hydrological data, May, August, and September are defined as the dry season, wet season and medium season, respectively. Dahuofang reservoir provides drinking water and irrigation water for Fushun city and Shenyang city. The water quality of Dahuofang reservoir is an important factor to determine the safety of water consumption. Based on industry, mining, and agricultural production, the morphology and hydrology of the Hun River, the different types of land around the Dahuofang reservoir and the principle of isometric random sampling, 21 water sampling stations in the Hun River and 13 soil sampling stations around the Dahuofang reservoir were chosen to study the concentrations of Cr, Cu and Zn in water and soil along the Hun River on 5 May, 5 August, and 5 September, 2013 (Figs. 1, 2; Table 1). Each water sampling station was approximately 1 km from the others, and thus, the change in the concentrations of Cr, Cu and Zn can be described via distance. Water samples were collected from the riverside at a depth of approximately 30 cm below the surface water using acid-washed polyethylene containers. The containers were rinsed with distilled water and washed with river water three times before being filled with the water sample. Approximately 50 ml of each water sample was filtered and collected in a sample bottle, and then, 1% nitric acid (HNO_3) was added. The concentrations of Cr, Cu and Zn in the water sample were determined as previously described (Abdul et al. 2011) by inductively coupled plasma-mass spectrometry (ICP–MS). The quantification limit is 0.09 µg/L for the concentration of Cr, 0.09 µg/L for the concentration of Cu and 0.8 µg/L for the concentration of Zn for water sample. Each soil sampling station was approximately 3 km from the others, and thus, the change in the concentrations of Cr, Cu and Zn can be described via distance. Soil samples were collected from different types of land around the Dahuofang reservoir at four depths of 0–10, 10–20, 30–40, and 40–50 cm and then stored in polyethylene containers. The soil samples were ground after drying in shade naturally, pulverized using a plastic hammer, and passed through a 0.149-mm sieve. The concentrations of Cr, Cu and Zn in the soil were measured by the mixed acid digestion method with HNO_3–$HClO_4$–HF. The quantification limit is 5 mg/kg for the concentration of Cr, 2 mg/kg for the concentration of Cu and 0.4 mg/kg for the concentration of Zn for soil sample. Statistical analysis was performed using principal component analysis (PCA) and the statistical significance. PCA is a statistical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of linearly uncorrelated variables called principal components (Zhang et al. 2012).

Results and Discussion

The concentrations of Cr, Cu, and Zn in Hun River were 0.0010 to 0.1298, 0.0057 to 0.1533 and 0.0162 to 0.5004 mg/L, respectively. The concentrations of Cr, Cu, and Zn in soil from around the Dahuofang reservoir were 0.0033 to 0.2149, 0.0054 to 0.2218 and 0.0135 to 0.3544 mg/g, respectively (Figs. 3, 4, 5, 6, 7, 8). Compared with the results of Ma and Wu, the concentrations of Cr, Cu, and Zn in water and soil along the Hun River had shown growing trend and caused ecological toxicity at some sampling stations (Ma et al. 2014a; Wu et al. 2011a).

Figures 3, 4 and 5 show the mean concentrations of Cr, Cu and Zn in the Hun River during the various seasons. All highest mean concentrations of Cr, Cu and Zn in the Hun River were obtained during the dry season, the lowest mean concentrations of Cr and Zn in the Hun River were obtained during the medium season, and the lowest mean concentration of Cu in the Hun River was obtained during the wet season. However, Ma obtained that the contents of heavy metals in surface water from the upper reaches of Hun River during the wet season were higher than those during normal and dry season (Ma et al. 2014a). Figures 6, 7 and 8 show the mean concentrations of Cr, Cu and Zn in soil from around the Dahuofang reservoir during the various seasons. All the highest mean concentrations of Cr, Cu and Zn in soil from around the Dahuofang reservoir were obtained during the medium season.

The concentrations of Zn in the Hun River at Y7 and Y21 were significantly different from the other sample stations ($p < 0.01$, Table 2). The concentrations of Cr, Cu

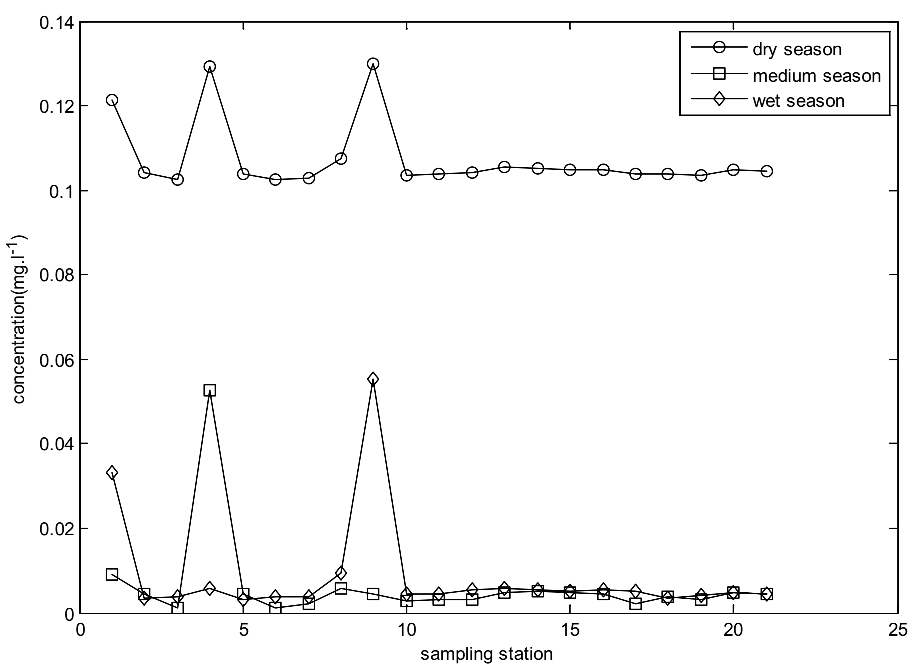

Fig. 3 The mean concentrations of Cr in the Hun River during different seasons

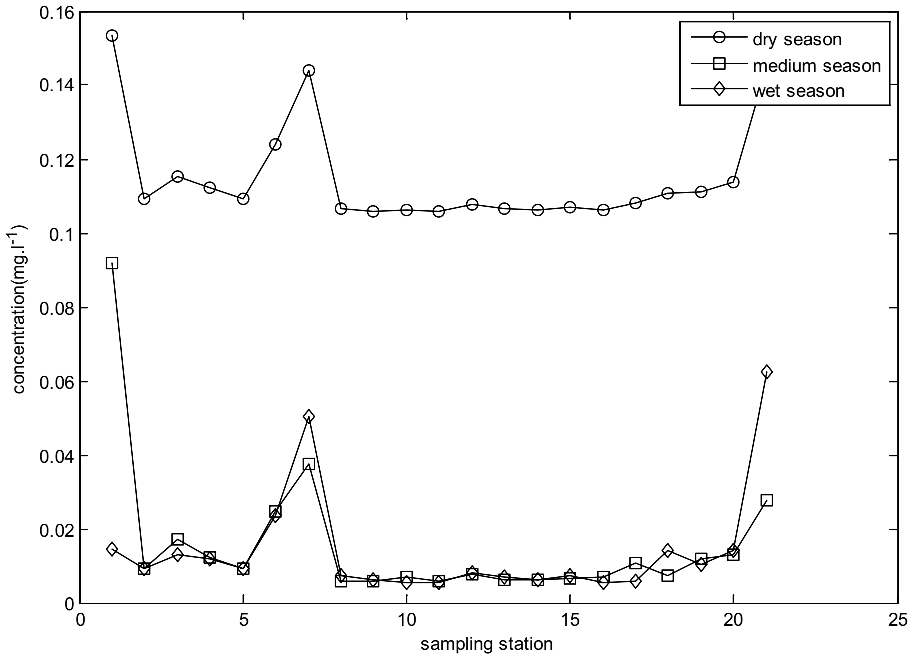

Fig. 4 The mean concentrations of Cu in the Hun River during different seasons

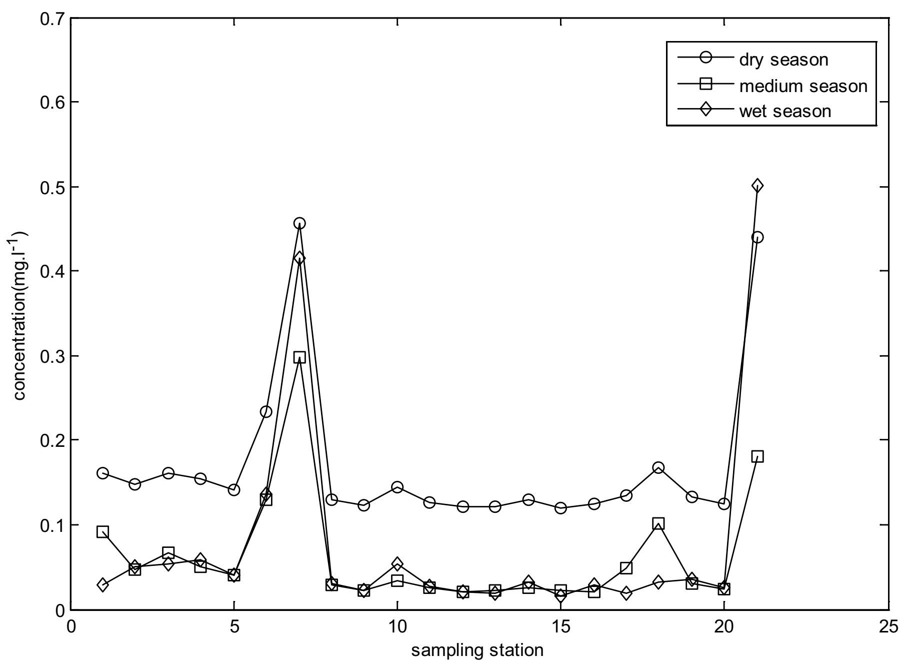

Fig. 5 The mean concentrations of Zn in the Hun River during different seasons

and Zn in the Hun River during the dry season were significantly different from those during the medium season and wet season ($p<0.01$, Table 3). The concentration of Cr in soil from the forest land was significantly different from that from the other types of land ($p<0.05$), and no significant difference was found at different types of land around the Dahuofang reservoir ($p>0.01$). The concentration of Cu in soil from the forest land was significantly different from that from the other types of land ($p<0.05$), especially from farm land ($p<0.01$). However, the concentration of Zn in soil from farm land was significantly different from that from uncultivated land and forest land ($p<0.05$), especially from uncultivated land ($p<0.01$, Table 4). The concentrations of Cr and Cu in soil from the different types of land around the Dahuofang reservoir during the medium season were significantly different from those during the dry season ($p<0.05$) but were not significantly different during the different seasons

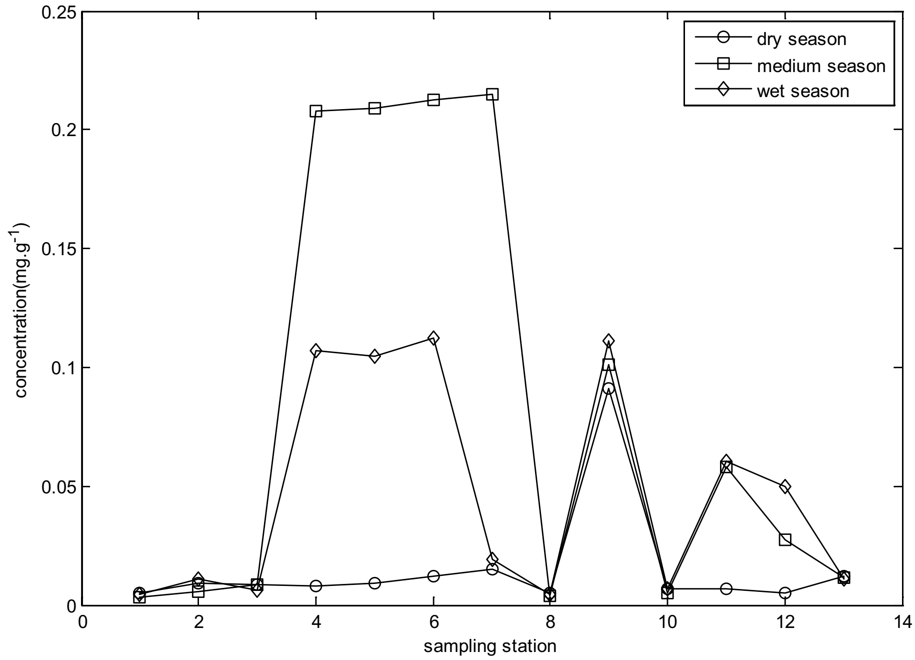

Fig. 6 The mean concentrations of Cr in soil from around the Dahuofang reservoir during different seasons

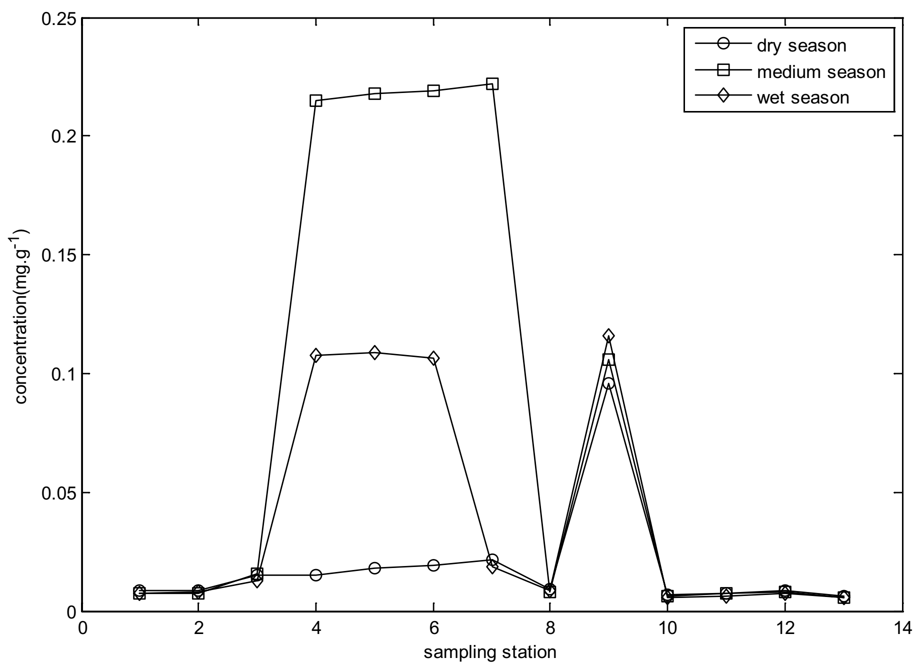

Fig. 7 The mean concentrations of Cu in soil from around the Dahuofang reservoir during different seasons

($p > 0.01$, Table 5). The concentrations of Zn in soil from the different types of land around the Dahuofang reservoir showed no significant difference during the different seasons ($p > 0.05$, Table 5). The significant difference revealed that the concentrations of Cr, Cu and Zn in water and soil along the Hun River changed dramatically depending on the station, season and type of land, which may aid in the effective control of heavy metal pollution along the Hun River. For example, we should adopt different methods to control heavy metal pollution during different seasons.

Table 2 shows that the concentration of zinc was 0.3898 mg/L at sampling station Y7 and 0.3741 mg/L at sampling station Y21. The high concentrations of zinc at Y7 and Y21 may be attributed to zinc mine residues and fertilizer. Since the Cr, Cu and Zn in Hun River were hard to be discharged during the dry season, the concentrations of Cr, Cu and Zn in the Hun River during the dry

Fig. 8 The mean concentrations of Zn in soil from around the Dahuofang reservoir during different seasons

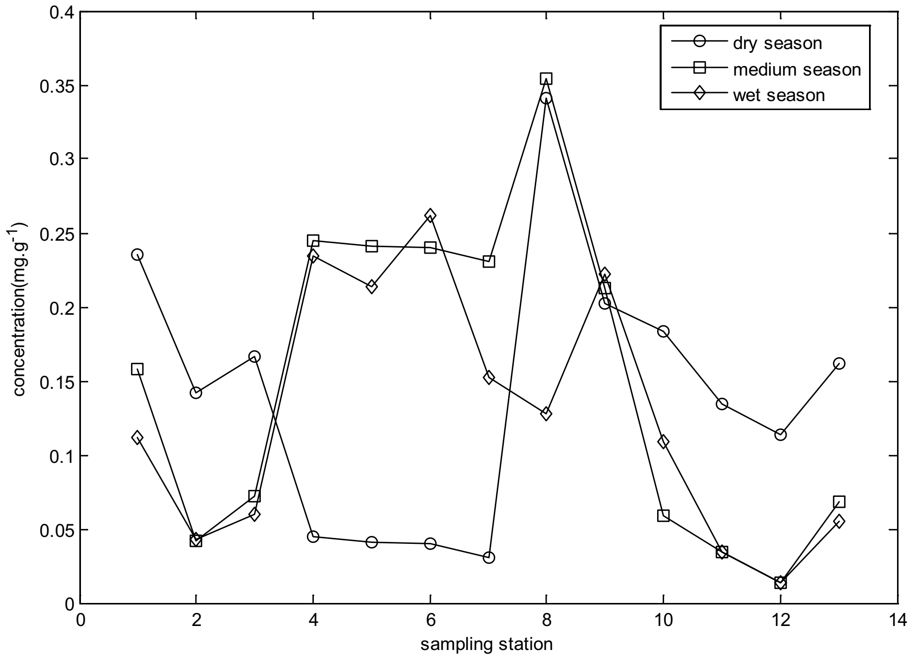

Table 2 Statistical results of the mean concentrations of Zn at different sampling stations in the Hun River (mg/L)

Station	Zn	Station	Zn	Station	Zn
Y1	0.0936Aa	Y2	0.0817Aa	Y3	0.0940Aa
Y4	0.0881Aa	Y5	0.0742Aa	Y6	0.1664Aa
Y7	0.3898Bb	Y8	0.0633Aa	Y9	0.0563Aa
Y10	0.0773Aa	Y11	0.0597Aa	Y12	0.0540Aa
Y13	0.0548Aa	Y14	0.0626Aa	Y15	0.0527Aa
Y16	0.0587Aa	Y17	0.0676Aa	Y18	0.1003Aa
Y19	0.0665Aa	Y20	0.0584Aa	Y21	0.3741Bb

The lowercase letters after the figures indicate a α = 0.05 level significant difference, while the capital letters indicate a α = 0.01 level significant difference

Table 3 Statistical results of the mean concentrations of Cr, Cu and Zn in water from the Hun River during different seasons (mg/L)

Season	Cr	Cu	Zn
Dry season	0.1074Bb	0.1150Bb	0.1711Bb
Medium season	0.0063Aa	0.0158Aa	0.0637Aa
Wet season	0.0085Aa	0.0142Aa	0.0786Aa

The lowercase letters after the figures indicate a α = 0.05 level significant difference, while the capital letters indicate a α = 0.01 level significant difference

season were higher than those during the medium season and wet season (Table 3). Table 4 shows that zinc was the most abundant heavy metal in the soil from different types of land around the Dahuofang reservoir. The mean concentration of zinc was 0.1297 mg/g in the flood land,

Table 4 Statistical results of the mean concentrations of Cr, Cu and Zn in soil from different types of land around the Dahuofang reservoir (mg/L)

Type of land	Cr	Cu	Zn
Flood land	0.0320Aa	0.0357ABa	0.1297ABab
Forest land	0.1010Ab	0.1057Bb	0.1612ABb
Uncultivated land	0.0373Aa	0.0403ABa	0.2013Bb
Farm land	0.0269Aa	0.0069Aa	0.0700Aa

The lowercase letters after the figures indicate a α = 0.05 level significant difference, while the capital letters indicate a α = 0.01 level significant difference

Table 5 Statistical results of the mean concentrations of Cr, Cu and Zn in soil from around the Dahuofang reservoir during different seasons (mg/L)

Season	Cr	Cu	Zn
Dry season	0.0149Aa	0.0185Aa	0.1413Aa
Medium season	0.0822Ab	0.0804Ab	0.1517Aa
Wet season	0.0468Aab	0.0399Aab	0.1261Aa

The lowercase letters after the figures indicate a α = 0.05 level significant difference, while the capital letters indicate a α = 0.01 level significant difference

0.1612 mg/g in the forest land, 0.2013 mg/g in uncultivated land and 0.07 mg/g in farm land. The high concentrations of zinc in the different types of land around the Dahuofang reservoir may be attributed to mining activities and excess zinc sulfate in fertilizers (Wu et al. 2011b). Since heavy metals were introduced into the soil around the Dahuofang reservoir by irrigation water from the Hun River, the concentrations of Cr, Cu and Zn in the soil around the Dahuofang reservoir during the medium season were higher than those during the dry season and wet season (Table 5). However, Ma et al. (2015) obtained that the heavy metal concentrations in sediments during the dry season were higher than those during the medium season and wet season. These results showed that mining activities, industrial effluent discharge and agricultural activity were responsible for Cr, Cu and Zn pollution along the Hun River.

Principal component analysis has previously been used to study the distribution and accumulation of heavy metals in river and soil (Singh et al. 2015; Li et al. 2006; Ma et al. 2015; Kikuchi et al. 2009). In this study, principal component analysis was employed to build pollution indexes for Cr, Cu and Zn in the water and soil along the Hun River. The first principal component and the second principal component of the pollution indexes of heavy metals in the Hun River are defined by PIW_1 and PIW_2, respectively. The first principal component and the second principal component of the pollution indexes of heavy metals in the soil from around the Dahuofang reservoir are defined by PIS_1 and PIS_2, respectively.

We obtain the pollution indexes of heavy metals in water and soil along the Hun River by using principal component analysis.

$$PIW_1 = 0.5963\mathrm{Cr} + 0.6432\mathrm{Cu} + 0.4803\mathrm{Zn} \quad (1)$$

and

$$PIW_2 = -0.4992\mathrm{Cr} - 0.1714\mathrm{Cu} + 0.8493\mathrm{Zn}. \quad (2)$$

The cumulative proportion rates of formulas (1) and (2) were 77.2% and 98.6%, respectively.

$$PIS_1 = 0.6188\mathrm{Cr} + 0.6330\mathrm{Cu} + 0.4653\mathrm{Zn} \quad (3)$$

and

$$PIS_2 = -0.3801\mathrm{Cr} - 0.2771\mathrm{Cu} + 0.8825\mathrm{Zn}. \quad (4)$$

The cumulative proportion rates of formulas (3) and (4) were 78.27% and 99.32%, respectively. For the pollution indexes of Cr, Cu and Zn in the Hun River, the first principal component was positively determined by the concentrations of Cr, Cu and Zn, and the second principal component was negatively determined by the concentrations of Cr and Cu and positively determined by the concentration of Zn. For the pollution indexes of Cr, Cu and Zn in soil around the Dahuofang reservoir, the first principal component was positively determined by the concentrations of Cr, Cu and Zn, and the second principal component was negatively determined by the concentrations of Cr and Cu and positively determined by the concentration of Zn. PIW_2 and PIS_2 were hard to evaluate the heavy metal pollution level in research area. We defined PIW_1 and PIS_1 as the pollution index in Hun river basin. Since the coefficients in formula (1) and (3) were all positive, we used the pollution index in Hun river basin to evaluate the heavy metal pollution level. According to the results of the pollution index in Hun river basin, we know that the potentially toxic levels of Cr, Cu and Zn may occur frequently at Y7 in the Hun River, X1 in the flood land, X7 in the forest land, X8 in uncultivated land and X13 in farm land. In fact, the pollution indexes of Cr, Cu and Zn in the water and soil along the Hun River can be extended to a larger research area or be used to evaluate compound heavy metal pollution. Therefore, the pollution indexes of Cr, Cu and Zn in water and soil clearly contribute to the further understanding of heavy metal pollution in the natural environment.

Mining is an economically important industry along the Hun River, including copper mines, zinc mines, coal mines, etc. Mining activities, metallurgy and manufacturing contribute large amounts of heavy metals to water and soil along the Hun River (Guo and He 2013; Wang et al. 2013). The management of mining area and industrial area is the primary task to prevent the heavy metal pollution in research area. The sources of heavy metal pollution, caused by the domestic sewage, the abuse of fertilizers and livestock and poultry, should be reduced. In addition, we may adopt new technology and ways to remedy the heavy metal contaminated areas. For example, we may use special aquatic plants or adsorption medium to remove the heavy metal pollution along the Hun River. Since rainfall has a large seasonal variation along the Hun River, the accumulation and behavior of Cr, Cu and Zn in water and soil along the Hun River may be complicated by the above processes and show significant variation during different seasons. That is to say, the concentrations of Cr, Cu and Zn in water and soil along the Hun River may be affected by rainfall and runoff. It should be noted that the heavy metals in sediments and aquatic and terrestrial organisms along the Hun River should be investigated. This investigation is left for future work. According to the National Food Safety Standard of China (GB 2762-2017) and Chinese Dietary Reference Intakes (2016), it is clear that aquatic life and humans are threatened by the distribution and accumulation of heavy metals in water and soil along the Hun River. We must enact strict policy and pollution control strategies to ensure that the water and soil along the Hun River meet the natural environment standard for the health of aquatic life and humans.

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References

Abdul RM, Mutnuri L, Dattatreya PJ, Mohan DA (2011) Assessment of drinking water quality using icp-ms and microbiological methods in the bholakpur area, hyderabad, india. Environ Monit Assess 184(3):1581–1592

Akbulut NE, Tuncer AM (2011) Accumulation of heavy metals with water quality parameters in Kizilirmak River basin (Delice River) in Turkey. Environ Monit Assess 173(1–4):387–395

Arunakumara K K I U, Walpola B C, Yoon M H (2013) Current status of heavy metal contamination in Asias rice lands. Rev Environ Sci Biotechnol 12(4):355–377

Diagomanolina V, Farhanga M, Ghazi-Khansaria M et al (2004) Heavy metals (Ni, Cr, Cu) in the Karoon waterway river, Iran. Toxicol Lett 151(1):63–68

Fekri M, Kaveh S (2013) Heavy metal accumulation in soil after application of organic wastes. Arab J Geosci 6(2):463–467

Guo R, He X (2013) Spatial variations and ecological risk assessment of heavy metals in surface sediments on the upper reaches of Hun River, Northeast China. Environ Earth Sci 70(3):1083–1090

Hu C, Su D (2011) Application of comprehensive water quality identification index in water quality assessment of Hun River. Ecol Environ Sci 20(1):186–192

Kikuchi T, Furuichi T, Hai HT et al (2009) Assessment of heavy metal pollution in river water of Hanoi, Vietnam using multivariate analyses. Bull Environ Contam Toxicol 83(4):575–582

Li Y, Yu ZM, Song XX et al (2006) Application of principal component analysis (PCA)for the estimation of source of heavy metal contamination in Marine Sediments. Environ Sci 27(1):137–141

Lv CW, He J, Fan QY et al (2011) Accumulation of heavy metals in wild commercial fish from the Baotou urban section of the Yellow River, China. Environ Earth Sci 62(4):679–696

Ma YQ, Shi Y, Qin YW et al (2014a) Temporal-spatial distribution and pollution assessment of heavy metals in the upper reaches of Hunhe River (Qingyuan section), Northeast China. Environ Sci 35(1):108–116

Ma X, Zuo R, Wang JS et al (2014b) Spatial distribution and sources of heavy metals in soils from alluvial and diluvial fan of Hun River in Shenyang. Res Environ Sci 27(11):1298–1305

Ma YQ, Qin YW, Zheng BH et al (2015) Seasonal variation of enrichment, accumulation and sources of heavy metals in suspended particulate matter and surface sediments in the Daliao river and Daliao river estuary, Northeast China. Environ Earth Sci 73(9):5107–5117

Qian Y, Zheng MH, Gao L et al (2005) Heavy metal contamination and its environmental risk assessment in surface sediments from lake Dongting, People's Republic of China. Bull Environ Contam Toxicol 75(1):204–210

Singh S, Raju NJ, Nazneen S (2015) Environmental risk of heavy metal pollution and contamination sources using multivariate analysis in the soils of Varanasi environs. India. Environ Monit Assess 187(6):1–12

Wang C, Shen Z, Li X et al (2004) Heavy metal contamination of agricultural soils and stream sediments near a copper mine in Tongling, People's Republic of China. Bull Environ Contam Toxicol 73(5):862–869

Wang T, Zhang F, Wang H et al (2013) Spatial distribution and ecological risk assessment of heavy metals in soils of the Hun River alluvial-plain fan in Shenyang, Liaoning, China. J Food Agric Environ 11(3):1606–1610

Wu XL, Yang YL, Tang QF et al (2011a) Ecological risk assessment and source analysis of heavy metals in river waters, groundwater along river banks, and river sediments in Shenyang. Chin J Ecol 30(3):438–447

Wu XL, Yang YL, Xu Q et al (2011b) Evaluations of heavy metal pollution status in surface soil adjacent to the rivers and irrigation channel in Shenyang, China. J Agro-Environ Sci 30(2):282–288

Zhang HL, Sun LN, Zhao GP (2012) Sources of heavy metals in surface water from Hunhe River by principal component analysis. J Shenyang Univ 24(5):5–9