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Spatial Distribution and Seasonal Variations of Heavy Metal Contamination in Surface Waters of Liaohe River, Northeast China

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Abstract: Heavy metal pollutants are a worldwide concern due to slow decomposition, biocondensation, and negative effects on human health. We investigated seasonal and spatial variations of the five heavy metals and evaluated their health risk in the Liaohe River, Northeast China. A total of 324 surface water samples collected from 2009 to 2010 were analyzed. Levels (high to low) of heavy metals in the Liaohe River were: zinc (Zn) > chromium (Cr) > copper (Cu) > cadmium (Cd) > mercury (Hg). Spatial and seasonal changes impacting concentrations of Cu and Zn were significant, but not significant for Cr, Cd and Hg. The highest concentrations of heavy metals were: Hg at Liuheqiao, Cu at Fudedian, Zn at Tongjiangkou, Cr at Mahushan, and Cd at Shenglitang. The highest concentrations of Hg and Cr were found in the wet period, Cu and Cd in the level period, and Zn in the dry period. The surface water of a tributary was an important accumulation site for heavy metals. Health risks from carcinogens and non-carcinogens increased from upstream to downstream in the mainstream of the Liaohe River. The total health risk for one person in the Liaohe River exceeded acceptable levels. The total health risk was the greatest during the wet period and least in the dry period. Among the five heavy metals in the Liaohe River, Cr posed the greatest single health risk.

Keywords: heavy metal; metal contamination; health risk; Liaohe River

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1 Introduction

Rapid population growth and economic development have increased the amounts of pollutants entering rivers and these degrade the water quality. Heavy metals are important pollutants that often accumulate in surface water (Pertsemli and Voutsa, 2007; Krishna *et al*., 2009; Li and Zhang, 2010; Memet, 2013). Heavy metals from natural sources are typically present in very low concentrations and are widely distributed in ecosystems such as air, water and soil. Heavy metals can be transported and transformed in aquatic systems by means of natural and anthropogenic sources such as direct input, atmospheric deposition, agricultural activities, and surface water runoff (Nriagu, 1989; Demirak *et al*., 2006; Macklin *et al*., 2006; Li *et al*., 2008). In areas where economic activities are intensive, such as industrial, agricultural and mining locations, the heavy metal contamination is typically widespread. Therefore, heavy metal levels can often exceed the natural background in aquatic environments (Bryan and Langston, 1992; Obasohan *et al*., 2006). Although there are many types of river pollutants, heavy metals are of greatest concern due to their slow decomposition under natural condi-

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tions and their biocondensation by aquatic organisms (Sin *et al*., 2001; Li *et al*., 2008; Obasohan *et al*., 2008; Rauf *et al*., 2009; Liu and Li, 2011; Varol, 2011). In many countries, water polluted by heavy metals is used for irrigating farms and other anthropogenic purposes. In these situations, crops and aquatic organisms may be exposed to elevated levels of the heavy metals (Kalay and Canli, 2000; Wajahat *et al*., 2006; Suresh *et al*., 2012; Xiao *et al*., 2012; Tang *et al*., 2013; Taweel *et al*., 2013;), negatively effecting human health. Research on levels and fates of heavy metals in aquatic environments is therefore essential.

Many studies have been conducted on the heavy metals in rivers. Memet (2013) evaluated the concentrations of heavy metals in the Kralkizi, Dicle, and Batman dam reservoirs within the Tigris River Basin. Heavy metal contamination of surface waters and bed sediments of the Haihe River Basin was studied by Tang *et al*. (2013). The distribution and contamination risk of dissolved trace metals in surface waters of the Yellow River Delta was reported by Song *et al*. (2013). Zhang *et al*. (2008a) assessed heavy metal pollution in the surface sediments of the Liaohe River using a geoaccumulation index. Deng *et al*. (2011) discussed sediment quality criteria and recommended values of four heavy metals using the Equilibrium Partitioning approach. Bu *et al*. (2014) assessed the ecological risk of heavy metals and toxicity characterization of surface sediments in the Liaohe River. These studies focused on heavy metal distribution and sources of sediments. Less work has been done on fluctuating levels, and corresponding health risks, of heavy metals in surface waters during different time periods.

The Liaohe River is an important river in Northeast China. With industrial development in the Liaohe River Basin, wastewater containing heavy metals enters into both the mainstream and the tributary. This has caused negative effects on the river and the surrounding environment. We studied pollution levels of five heavy metals in the Liaohe River in relation to spatial distribution and seasonal variations and evaluated the degree of health risk. The characteristics of the five heavy metals could be useful in future pollution management of the Liaohe River.

2 Materials and Methods

2.1 Study area

The Liaohe River, the seventh longest river in China, is located in Northeast China. It flows through Hebei Province, Inner Mongolia Autonomous Region, Jilin Province and Liaoning Province, and enters to the Bohai Sea at last in Panjin City of Liaoning Province (Tian, 2005; Li, 2008). In this paper, the study area was the branch of the Liaohe River in Liaoning Province. It provides freshwater to Shenyang City, Tieling City and Panjin City for drinking, industrial and crop production. With the development of the industries around the area, more and more wasted water were discharged into the water body and exerted negative effects on the safety of the water environment (Chen *et al*., 2007). The dry period and the wet period were from December to April and from July to August, respectively. The other mouths were the level period in the study area.

A total of 15 sampling stations were selected in the mainstream and tributaries of the Liaohe River (Fig. 1). Eight stations were in the mainstream, viz. Fudedian (FDD), Sanhetun (SHT), Zhuershan (ZES), Mahushan (MHS), Hongmiaozi (HMZ), Panjinxingan (PJXA), Shuguangdaqiao (SGDQ) and Zhaoquanhe (ZQH), and seven stations were in the tributaries, viz. Tongjiangkou (TJK), Qingliao (QL), Dongdaqiao (DDQ), Huanghezi (HHZ), Jiumenqiao (JMQ), Liuheqiao (LHQ) and Shenglitang (SLT). ZES represents the inflow monitoring section from Tieling City to Shenyang City. HMZ represents the inflow from Shenyang City to Panjin City. ZQH represents the contamination level of the Liaohe River flowing into the Bohai Sea. SHT, ZES and SGDQ sampling stations reflect the heavy metals contamination level after the main tributaries merging into the main river. The data of the heavy metals contamination of the surface water functioned as monitoring the quality of sewage, industrial effluents, and urban or rural runoff. Therefore, we carried out a typical environmental monitoring plan to study the heavy metals contamination in the surface water of the Liaohe River from 2009 to 2010.

2.2 Sample collection and analytical methods

Water samples were collected once in each month from January to December during 2009–2010 in the 15 sites. At each station, three samples were collected from a depth of 30.48 cm below the surface using acid-leached polythene bottles and preserved with Conc. HNO_3 and then refrigerated to 4℃ pending analysis (Ayenimo *et al*., 2005; Kar *et al*., 2008). The pH of water samples

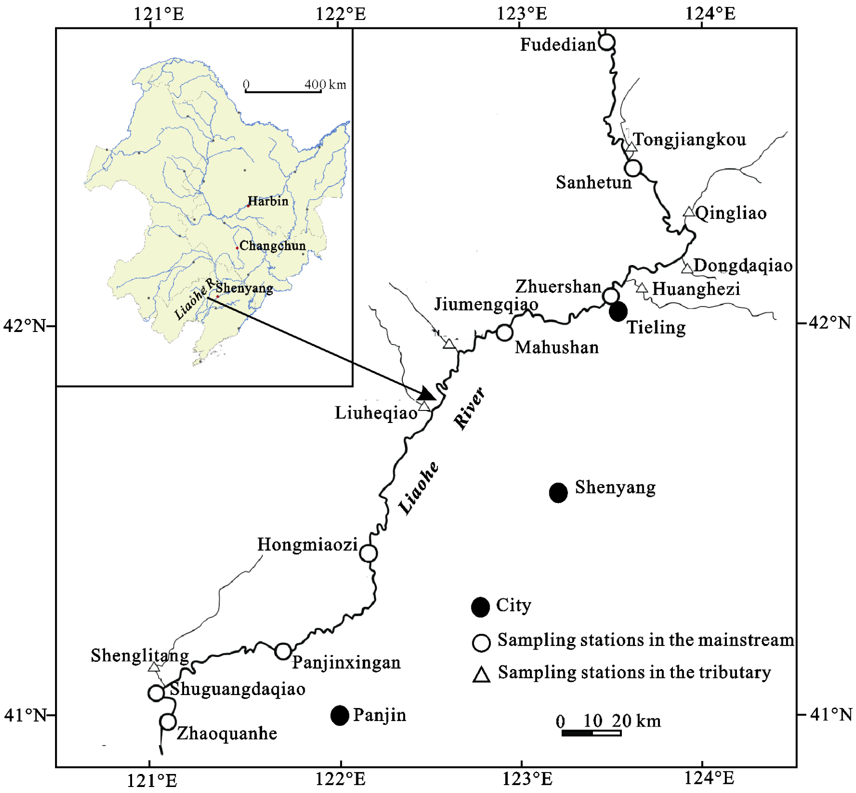

Fig. 1 Locations of monitoring stations in Liaohe River

was determined immediately before preservation using pH-meter with electronic glass electrode (WTW.1-Photo Flex Turb, Germany). The samples were diluted by bidistilled water. The analysis of the five heavy metals, viz. Cu, Hg, Zn, Cd, and Cr, was carried out by atomic absorption spectrometry method using atomic absorption spectrophotometer (VARIAN AA220, American) and the standard solutions of the respective metal were used for quantifying the samples (Diagomanolin *et al.*, 2004).

2.3 Health risks of heavy metals

The effects of the heavy metals to the human being could be measured by drinking water approach. The health risks consist of chemical carcinogens and chemical non-carcinogens. The carcinogens considered in this paper were Cd and Cr, while Cu, Hg and Zn were non-carcinogens.

The model of health risk from the chemical carcinogens was as follows (Zhang *et al.*, 2008b; Li and Liu, 2009; Zou *et al.*, 2009):

$$Rc = \sum_{i=1}^{k} Rc_i \tag{1}$$

$$Rc_i = [1 - \exp(-D_i \cdot Q_i)]/70 \tag{2}$$

where Rc was the health risks from chemical carcinogens; Rc_i was the average annual cancer risk for individual through drinking water channels of chemical carcinogen i; D_i (mg/(kg·d)) was the personal exposure dose of 1 U/kg everyday through drinking water channels of chemical carcinogens i; Q_i (mg/(kg·d)) was the strength coefficient of carcinogenic effect through drinking water channels of chemical carcinogen i, and 70 was the average life span for human. D_i can be performed as follows:

$$D_i = 2.2C_i/70 \tag{3}$$

where 2.2 L was the amount of water intake of an adult; C_i was the concentration of chemical carcinogens; and 70 kg was the average weight of an adult in China.

The model of health risk from the chemical non- carcinogens was as follows:

$$Rn = \sum_{i=1}^{k} Rn_i \tag{4}$$

$$Rn_i = (D_i \times 10^{-6}/RfD_i)/70 \tag{5}$$

where Rn was the health risks from chemical non-carcinogens; Rn_i was the average annual cancer risk for individual through drinking water channels of chemical non-carcinogens i; RfD_i (mg/(kg·d)) was the reference dose through drinking water channels of chemical carcinogen i; and 70 was the average life span for human.

We assumed that toxic action to human health of all poisonous materials were in a dependent way. So the total health risk (Rs) in water environment was calculated according to the following equation:

$$Rs = Rc + Rn \tag{6}$$

Strength coefficients for chemical carcinogens and reference doses for non-carcinogens by drinking water approach are showed in Table 1 (Su *et al.*, 2006; Li and Liu, 2009; Kai *et al.*, 2010).

Table 1 Strength coefficients of heavy metals through drinking water approach (mg/(kg·d))

Cd	Cr	Cu	Hg	Zn
6.1000	41.0000	0.0050	0.0003	0.0210

2.4 Statistical analysis

The obtained data were applied to statistical analysis on testing the variance (ANOVA) and correlation among all the parameters applying SPSS 15.0 for windows. EXCEL2007 was used to plot the experimental data and then the map of sampling sites was drawn. The results of all indices represent the average values of the three samples for each site.

3 Results and Discussion

3.1 Variations of pH

The range of water sample pH values was from 6.98 to 8.22. The overall mean (7.86) was slightly alkaline. Mean pH values varied from 7.73 in the dry period to 7.94 in the level period (Table 2). The lowest pH value always occurred in the dry period except for SGDQ, ZQH and JMQ. No significant difference was noted in the pH values observed during the level period and the wet period. The variations in pH due to change in sample location were not significant except for LHQ. The mean pH was the highest in the mainstream of the Liaohe River while it was lowest in the tributary. The mean pH values in the mainstream were lowest during the dry period, higher during the wet period, and highest in the level period. Similar results were also observed by Guo (2009) in the Liaohe River Basin. The pH variations were the same in the tributaries and in the Liaohe River.

The pH affects the solubility of heavy metals, influences pathogen survival, and is one of most important indicators of water quality in aquatic ecosystems (Jonnalagadda and Mhere, 2001; Khan *et al.*, 2013). The values of pH are controlled by dissolved carbon dioxide, and influenced by temperature, flow rate, and acidic materials discharged into the river. In some locations, the tributary stream was contaminated by sewage from industries and farms. Many contaminants, such as acidic materials, entered into the river mainstream from the tributary. Some acidic materials were volatile and their

Table 2 Mean value of pH in surface water of Liaohe River in different sites and different periods

Season	Mainstream								
	FDD	SHT	ZES	MHS	HMZ	PJXA	SGDQ	ZQH	Average
Dry period	7.62	7.61	7.57	7.67	7.64	7.95	8.04	8.22	7.79
Level period	7.98	7.93	7.91	7.88	7.97	8.03	7.96	7.85	7.94
Wet period	7.98	8.03	7.87	7.75	7.71	8.20	7.79	7.92	7.91
Average	7.86	7.86	7.78	7.77	7.78	8.06	7.93	8.00	7.88

Season	Tributary								Liaohe River
	TJK	QL	DDQ	HHZ	JMQ	LHQ	SLT	Average	
Dry period	7.79	7.57	7.75	7.50	7.86	6.98	7.89	7.62	7.73
Level period	7.97	7.82	7.96	7.95	8.03	7.91	8.03	7.95	7.94
Wet period	8.03	7.91	7.84	7.83	7.62	7.83	8.05	7.87	7.90
Average	7.93	7.77	7.85	7.76	7.84	7.57	7.99	7.81	7.86

Notes: FDD (Fudedian), SHT (Sanhetun), ZES (Zhuershan), MHS (Mahushan), HMZ (Hongmiaozi), PJXA (Panjinxingan), SGDQ (Shuguangdaqiao) and ZQH (Zhaoquanhe) were the monitoring sections in the mainstream, and TJK (Tongjiangkou), QL (QingliaoL), DDQ (Dongdaqiao), HHZ (Huanghezi), JMQ (Jiumenqiao), LHQ (Liuheqiao) and SLT (Shenglitang) were the monitoring sections in the tributary flow rate was larger in the mainstream than in the tributary. Thus, the pH in the mainstream was higher than in other areas. The solubility of gases generally decreased with increasing water temperature. There was more carbon dioxide dissolved in water in the dry period and the concentration of carbonic acid in the dry period was higher than in other periods. The dilution effect of the river was reduced with the decreasing flow rate of water in the dry period. That was one reason why pH was the lowest in the dry period, higher in the wet period, and highest in the level period.

3.2 Seasonal variations of heavy metals contamination

Cu, Hg, Zn, Cd, and Cr in the Liaohe River water samples were analyzed. The mean concentrations of the five heavy metals in the dry period (low water season), wet period (abundant water season), and level period (level water season) are presented in Table 3, Table 4 and Fig. 2, respectively. Heavy metals were detected in most water samples. Zn and Cu, as essential micronutrients, were detected in 216 samples. The Zn values ranged from 2.50×10^{-2} mg/L to 8.61×10^{-2} mg/L, with a mean concentration of 3.96×10^{-2} mg/L in the dry period, from 2.45×10^{-2} mg/L to 3.90×10^{-2} mg/L, with a mean concentration of 2.71×10^{-2} mg/L in the level period, and from 2.50×10^{-2} mg/L to 8.00×10^{-2} mg/L, with a mean concentration of 2.64×10^{-2} mg/L in the wet period. The Cu values ranged from 5.00×10^{-3} mg/L to 2.07×10^{-2} mg/L, with a mean concentration of 6.36×10^{-3} mg/L in

Table 3 Average concentration of heavy metals in mainstream of Liaohe River (mg/L)

Metal	Season	FDD	SHT	ZES	MHS	HMZ	PJXA	SGDQ	ZQH
Hg	Dry period	2.00E-05	2.00E-05	2.00E-05	2.88E-05	2.90E-05	2.50E-05	2.90E-05	2.00E-05
	Level period	2.00E-05	2.00E-05	2.00E-05	3.00E-05	3.00E-05	2.60E-05	2.60E-05	2.60E-05
	Wet period	2.00E-05	2.00E-05	2.00E-05	3.00E-05	3.00E-05	2.75E-05	3.50E-05	3.50E-05
Cu	Dry period	5.00E-03	5.00E-03	5.00E-03	2.07E-02	5.00E-03	5.00E-03	5.00E-03	5.00E-03
	Level period	3.17E-02	5.00E-03	5.00E-03	1.00E-02	1.10E-02	5.00E-03	5.00E-03	5.00E-03
	Wet period	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03
Zn	Dry period	2.50E-02	5.93E-02	4.00E-02	5.29E-02	3.17E-02	2.50E-02	2.50E-02	2.50E-02
	Level period	2.50E-02	3.31E-02	2.50E-02	2.45E-02	3.90E-02	2.50E-02	2.50E-02	2.50E-02
	Wet period	2.50E-02	2.50E-02	2.50E-02	2.50E-02	2.50E-02	2.50E-02	2.50E-02	2.50E-02
Cr	Dry period	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	1.94E-02	2.82E-02	2.85E-02
	Level period	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.23E-02	2.80E-02	2.75E-02
	Wet period	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.30E-02	3.11E-02	3.03E-02
Cd	Dry period	5.00E-04	5.00E-04	5.00E-04	4.36E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04
	Level period	5.00E-04	5.00E-04	5.00E-04	9.50E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04
	Wet period	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04

Notes: Sites′ name abbreviations are shown in table 2

Table 4 Average concentration of heavy metals in tributaries and Liaohe River (mg/L)

Metal	Season	TJK	QL	DDQ	HHZ	JMQ	LHQ	SLT	Liaohe River
Hg	Dry period	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.00E-05	3.00E-05	3.20E-05	2.34E-05
	Level period	2.00E-05	2.00E-05	2.00E-05	2.00E-05	3.00E-05	3.00E-05	3.50E-05	2.50E-05
	Wet period	2.00E-05	2.00E-05	2.00E-05	2.00E-05	3.00E-05	3.00E-05	3.50E-05	2.63E-05
Cu	Dry period	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	ND	5.00E-03	6.36E-03
	Level period	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	8.97E-03
	Wet period	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03
Zn	Dry period	8.61E-02	2.50E-02	2.50E-02	2.50E-02	2.50E-02	ND	2.50E-02	3.96E-02
	Level period	2.50E-02	2.50E-02	2.50E-02	2.50E-02	2.50E-02	2.50E-02	2.50E-02	2.71E-02
	Wet period	2.50E-02	2.50E-02	2.50E-02	2.50E-02	2.50E-02	8.00E-02	2.50E-02	2.64E-02
Cr	Dry period	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	ND	3.73E-02	8.16E-03
	Level period	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.50E-02	2.50E-02	3.35E-02	9.14E-03
	Wet period	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	3.70E-02	9.98E-03
Cd	Dry period	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04	ND	5.00E-04	4.94E-04
	Level period	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.47E-04
	Wet period	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04

Notes: ND means 'Not Detected'. Sites' name abbreviations are shown in table 2

the dry period, 5.00×10^{-3} mg/L to 3.17×10^{-2} mg/L, with a mean concentration of 8.97×10^{-3} mg/L in the level period, and with a mean concentration of 5.00×10^{-3} mg/L in the wet period. Hg, Cd, and Cr were detected in 320, 320 and 216 samples with concentrations within the ranges of 2.00×10^{-5}–3.20×10^{-5} mg/L, 4.36×10^{-4}–5.00×10^{-4} mg/L and 2.00×10^{-3}–3.73×10^{-2} mg/L, with overall means of 2.34×10^{-5} mg/L, 4.94×10^{-4} mg/L and 8.16×10^{-3} mg/L in the dry period, 2.00×10^{-5}–3.50×10^{-5} mg/L, 5.00×10^{-4}–9.50×10^{-4} mg/L and 2.00×10^{-3}–3.35×10^{-2} mg/L, with overall means of 2.50×10^{-5} mg/L, 5.47×10^{-4} mg/L and 9.14×10^{-3} mg/L in the level period, 2.00×10^{-5}–3.50×10^{-5} mg/L, 5.00×10^{-4}–5.00×10^{-4} mg/L and 2.00×10^{-3}–3.70×10^{-2} mg/L, with overall means of 2.63×10^{-5} mg/L, 5.00×10^{-4} mg/L and 9.98×10^{-3} mg/L in the wet period. The results showed that the mean concentrations of metals ranked (high to low): Zn > Cr > Cu > Cd > Hg. The concentrations of the five heavy metals were within the secure confine for crop production, but the concentration of Cr exceeded Environmental Quality Standards for Surface Water (GB3838-2002) in China (for drinking water, 0.00005 mg/L for Hg, 0.01 mg/L for Cu, 0.05 mg/L for Zn, 0.001 mg/L for Cd and 0.01 mg/L for Cr). However, there are numerous potential sources of Cr pollution in rivers. Cr can enter the river via atmospheric fallout, urban runoff, and effluents (Zhang *et al.*, 2008b).

The mean concentrations of Hg, Cu, Zn, Cr and Cd in the surface water of the Liaohe River in three different seasons ranged from 2.34×10^{-5} to 2.63×10^{-5} mg/L, from 5.00×10^{-3} to 8.97×10^{-3} mg/L, from 2.64×10^{-2} to 3.96×10^{-2} mg/L, from 8.16×10^{-3} to 9.98×10^{-3} mg/L, and from 4.94×10^{-4} to 5.47×10^{-4} mg/L, respectively (Fig. 2). Among the five heavy metals, the concentration of Cu and Zn impacted by seasonal change was significant, whereas in the case of Cr, Cd and Hg, the impact of seasonal change on concentration was not significant. The highest concentration of Hg and Cr was observed in the wet period while Cu and Cd were detected in the level period. The maximum concentration of Zn was observed in the dry period.

The seasonal variations of heavy metal contamination in the Liaohe River differed from the Tigris River Basin, where Cd, Cr and Cu levels were higher in the dry period, and higher levels of Zn occurred in the wet period (Memet, 2013). The concentrations of heavy metals were affected by the discharge of sewage and the flow rate of the Liaohe River. The discharges of sewage and industrial wastewater were almost constant in the different periods. However, the flow rate of the Liaohe River was greater in the wet period and less in the dry period. Therefore, the concentrations of heavy metals were greater in the dry period and lower in the wet period. The concentrations of heavy metals were impacted by the discharge of sewage and industrial wastewater, river flow rate, background levels of the heavy metals, and the chemical properties of the heavy metals. The solubility of the heavy metals was always higher in subacidity pH than in alkaline pH, and the pH in the dry period is lower. But the concentrations of Cu, Cr, Hg and Cd were often reduced due to their relatively lower release rate from the river sediments at the lower temperatures of the dry period. Those factors might all contribute to the seasonal changes in concentrations of heavy metals in the Liaohe River.

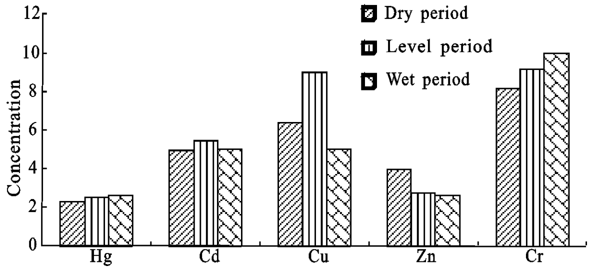

Fig. 2 Seasonal variations of heavy metal contaminations in Liaohe River. Hg, 10^{-5} mg/L; Cd, 10^{-4} mg/L; Cu, 10^{-3} mg/L; Zn, 10^{-2} mg/L; Cr, 10^{-3} mg/L

3.3 Spatial variations of heavy metal contaminations

The mean concentrations of Hg, Cu, Zn, Cr and Cd at 15 sites ranged from 2.00×10^{-5} to 3.60×10^{-5} mg/L, 5.00×10^{-3} to 1.66×10^{-2} mg/L, 2.50×10^{-2} to 4.89×10^{-2} mg/L, 2.00×10^{-3} to 3.60×10^{-2} mg/L and 5.00×10^{-4} to 6.93×10^{-4} mg/L (Table 5 and Table 6), respectively. Among the 15 monitoring stations, the highest mean concentration of Hg (3.60×10^{-5} mg/L) was observed at LHQ. Cu (1.66×10^{-2} mg/L) was highest at FDD, Zn (4.89×10^{-2} mg/L) at TJK, Cr (3.60×10^{-2} mg/L) at SLT, and Cd (6.93×10^{-4} mg/L) at MHS. The spatial differences in the concentrations of Zn, Cu and Cr were statistically different in the mainstream of the Liaohe River, and those of Zn and Cr were statistically different in the tributaries of the Liaohe River. The mean concentrations of Hg and Zn were higher in the tributary, and Cu and Cd were higher in the river mainstream.

The concentration of Cu was higher at the FDD and MHS sites than other six sites in the mainstream river. Jilin Province was the upstream of FDD and the Cu concentration may have been affected by the pollutants originating in Jilin Province. Many industrial effluents from Shenyang City discharged into the river near the MHS site. This could explain the higher Cu values at the MHS site. In contrast to the particulates of Zn, the particulates of Cu do not readily move long distances in rivers (Zeng *et al.*, 2008). There were no differences in

Table 5 Spatial changes of heavy metals in mainstream of Liaohe River (mg/L)

Metal	FDD	SHT	ZES	MHS	HMZ	PJXA	SGDQ	ZQH
Hg	2.00E-05	2.00E-05	2.00E-05	2.95E-05	2.96E-05	2.58E-05	2.88E-05	2.63E-05
Cu	1.66E-02	5.00E-03	5.00E-03	1.26E-02	7.61E-03	5.00E-03	5.00E-03	5.00E-03
Zn	2.50E-02	4.19E-02	3.09E-02	3.40E-02	3.37E-02	2.50E-02	2.50E-02	2.50E-02
Cd	5.00E-04	5.00E-04	5.00E-04	6.93E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04
Cr	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.13E-02	2.86E-02	2.84E-02

Notes: Sites′ name abbreviations are shown in table 2

Table 6 Spatial changes of heavy metals in tributaries of Liaohe River (mg/L)

Metal	TJK	QL	DDQ	HHZ	JMQ	LHQ	SLT
Hg	2.00E-05	2.00E-05	2.00E-05	2.00E-05	2.88E-05	3.60E-05	3.38E-05
Cu	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03	5.00E-03
Zn	4.89E-02	2.50E-02	2.50E-02	2.50E-02	2.50E-02	4.33E-02	2.50E-02
Cd	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04	5.00E-04
Cr	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	2.00E-03	3.60E-02

Notes: Sites′ name abbreviations are shown in table 2

Cu concentrations at other sites. The concentration of Zn in the mainstream river was higher in the SHT, MHS and HMZ sites than other five sites. The Zhaoshutai River, which flows into the mainstream of the Liaohe River before the SHT site, had a higher Zn value (4.89×10^{-2} mg/L) in TJK site, which likely caused the higher concentration of Zn at the SHT site. The Liu River, which flows into the mainstream of the Liaohe River before the HMZ site, had a higher Zn value (4.33×10^{-2}mg/L) in LHQ site. The wastewater of Shenyang City also discharged into the mainstream of theLiaohe River before the HMZ site. These pollutant discharges led to higher concentrations of Zn in the SHT, MHS and HMZ sites. The Raoyang River, which flows into the Liaohe River before the SGDQ site, had a high Cr value (3.60×10^{-2}mg/L) in SLT site. This helps explain why the concentration of Cr was significantly higher in SGDQ than at the other sites. Therefore, the tributary and the industrial effluents from Shenyang City were important sources of the heavy metals in the surface water of the Liaohe River.

3.4 Correlations among pH and heavy mental concentrations

The correlations among pH and heavy metal concentrations were determined and the results are shown in Table 7. There was a significant positive correlation between Cr and pH in the surface water of the Liaohe River, while Zn had a significant negative correlation with pH. This indicates that the concentration of Zn declined while the concentration of Cr increased with increasing pH. Correlation analysis of the five heavy metals (Hg, Cu, Zn, Cd and Cr) showed that Hg and Cd had a significant positive correlation with Cu, whereas Cd and Cr had a negative correlation with Zn. Analysis of heavy metal speciation in the aquatic environment helps to verify our findings about seasonal and spatial variations of the heavy metals (Kar *et al*., 2008).

3.5 Health risks of heavy metals

The annual health risk for one person is shown in Table 8. The most important carcinogen in the Liaohe River was Cr, and its concentration was usually an order of magnitude greater than that of Cd, which indicates that Cr was the major carcinogen pollutant in the Liaohe River. During monitoring of the mainstream, the health risk of Cr increased from upstream to downstream and it was greatest in the tributary at SLT. A trend of Cd concentrations was not pronounced among the monitoring stations but the concentration was greatest at MHS. *Rc* was affected by the concentration of Cr, and *Rc* increased from upstream to downstream in the mainstream in accordance with Cr. The greatest health risk was at the SLT monitoring station, which was the reason that *Rc* in SGDQ and ZQH was larger than other monitoring stations in the mainstream.

Table 7 Correlations among different heavy metals and pH of surface water of Liaohe River

	pH	Hg	Cu	Zn	Cd	Cr
pH	1					
Hg	0.008	1				
Cu	0.011	0.141^{*}	1			
Zn	-0.186^{**}	0.098	0.057	1		
Cd	0.110	0.000	0.265^{**}	-0.194^{**}	1	
Cr	0.257^{**}	0.072	–0.113	–0.146*	0.000	1

Notes: ** indicates that correlation is significant at the 0.01 level (2-tailed); * indicates that correlation is significant at the 0.05 level (2-tailed)

Table 8 Health risk from carcinogens and noncarcinogens for one person annually in different monitoring sites (1/yr)

Location	Cd	Cr	*Rc*	Hg	Cu	Zn	*Rn*	*Rs*
FDD	1.37E-06	3.68E-05	3.81E-05	2.99E-11	1.49E-09	5.35E-10	2.06E-09	3.81E-05
SHT	1.37E-06	3.68E-05	3.81E-05	2.99E-11	4.49E-10	8.97E-10	1.38E-09	3.81E-05
ZES	1.37E-06	3.68E-05	3.81E-05	2.99E-11	4.49E-10	6.60E-10	1.14E-09	3.81E-05
MHS	1.90E-06	3.68E-05	3.87E-05	4.42E-11	1.13E-09	7.28E-10	1.91E-09	3.87E-05
HMZ	1.37E-06	3.68E-05	3.81E-05	4.43E-11	6.83E-10	7.20E-10	1.45E-09	3.81E-05
PJXA	1.37E-06	3.87E-04	3.86E-04	3.87E-11	4.49E-10	5.35E-10	1.02E-09	3.89E-04
SGDQ	1.37E-06	5.17E-04	5.18E-04	4.30E-11	4.49E-10	5.35E-10	1.03E-09	5.18E-04
ZQH	1.37E-06	5.14E-04	5.15E-04	3.94E-11	4.49E-10	5.35E-10	1.02E-09	5.15E-04
TJK	1.37E-06	3.68E-05	3.81E-05	2.99E-11	4.49E-10	1.05E-09	1.53E-09	3.81E-05
QL	1.37E-06	3.68E-05	3.81E-05	2.99E-11	4.49E-10	5.35E-10	1.01E-09	3.81E-05
DDQ	1.37E-06	3.68E-05	3.81E-05	2.99E-11	4.49E-10	5.35E-10	1.01E-09	3.81E-05
HHZ	1.37E-06	3.68E-05	3.81E-05	2.99E-11	4.49E-10	5.35E-10	1.01E-09	3.81E-05
JMQ	1.37E-06	3.68E-05	3.81E-05	4.30E-11	4.49E-10	5.35E-10	1.03E-09	3.81E-05
LHQ	1.37E-06	3.68E-05	3.81E-05	5.39E-11	4.49E-10	9.27E-10	1.43E-09	3.81E-05
SLT	1.37E-06	6.48E-04	6.49E-04	5.05E-11	4.49E-10	5.35E-10	1.03E-09	6.49E-04

Cu and Zn were more important non-carcinogens than Hg in the Liaohe River. In the mainstream, the health risk of Cu and Zn decreased from the upstream to the downstream. The health risk of Cu was greatest at the FDD monitoring station while Zn was greatest at TJK. The *Rn* declined from upstream to downstream, and the largest value was found at FDD. Compared to carcinogens, the health risks of the non-carcinogens were four orders of magnitude smaller and the health risks of non-carcinogens were negligible.

The health risks from all carcinogens and non-carcinogens increased from upstream to downstream in the mainstream of the Liaohe River. The risk was greater at SLT than the other monitoring stations. Based on the greatest acceptable risk exposure level (5.00×10^{-5}/yr) recommended by International Commission on Radiological Protection (ICRP) (Su *et al*., 2006), there were four monitoring stations (PJXA, SGDQ, ZQH and SLT) where the health risk exceeded the ICRP acceptable level. Among the monitoring stations in the mainstream, the health risks from all carcinogens and non-carcinogens at the ZQH monitoring station were greatest. The upstream areas of the Liaohe River posed lesser risk and were safer places for inhabitants. Among the monitoring stations in the tributary stream, the health risks of carcinogens and non-carcinogens were greatest at SLT. SLT was an important source of the health risks of the Liaohe River and pollution control along this tributary would help reduce risks along the Liaohe River.

The annual health risk for one person exceeded the ICRP greatest acceptable level during the three seasons of the Liaohe River (Table 9). This was mainly due to carcinogen levels, especially Cr. The health risk was greatest in the wet period and least in the dry period. Heavy metal contamination would be expected to adversely affect the health of residents around the Liaohe River. There may be other carcinogens and non-carcinogens in the river in addition to the five heavy metals studied here. Therefore, the health risks posed by the Liaohe River are likely to be greater than the value estimated in this study. Based on our data, the pollution and the health risk issue of the Liaohe River should be addressed immediately.

4 Conclusions

We presented information on heavy metals in the surface water of the Liaohe River located in a heavily industrialized area in Northeast China. The pH levels were generally alkaline as well as it was within the secure confine

Table 9 Health risk for one person annually of different seasons in Liaohe River (1/yr)

Season	*Rn*	*Rc*	*Rs*
Wet period	1.05E-09	1.84E-04	1.84E-04
Level period	1.42E-09	1.69E-04	1.69E-04
Dry period	1.45E-09	1.51E-04	1.51E-04

for drinking and crop production. The mean concentration of heavy metals was in the following order (high to low): Zn > Cr > Cu > Cd > Hg. Spatial and seasonal changes of Cu and Zn concentrations were significant, while the seasonal changes of Cr, Cd and Hg were not significant. Hg and Zn levels were greater in the tributary, and Cu, Cr and Cd levels were higher in the mainstream. The highest concentrations of Hg and Cr occurred in the wet period, Cu and Cd in the level period, and Zn in the dry period. Among the five heavy metals, Hg and Cd were positively correlation with Cu, whereas Cd and Cr were negatively correlated with Zn. The Liaohe River water may be unsuitable for drinking due to excess Cr and other heavy metals. The relative health risk from all carcinogens and non-carcinogens increased from upstream to downstream in the mainstream of the Liaohe River. The total health risk for one person annually exceeded the ICRP acceptable level during the three study seasons. The risk was greatest in the wet period and least in the dry period. Cr posed the greatest health risk in the Liaohe River. Measures to remove the heavy metal load from industrial wastewater and renovation of sewage treatment plants should be established to reduce heavy metal pollution and to avoid further deterioration of the Liaohe River water quality.

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