

# Health Risk Assessment and Spatial Distribution Characteristic on Heavy Metals Pollution of Haihe River Basin

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### Abstract

The concentrations of carcinogenic risk substances of cadmium (Cd), chromium (Cr), arsenic (As) as well as noncarcinogenic risk substances of lead (Pb), mercury (Hg), Copper (Cu), zinc (Zn), ammonia (NH<sub>3</sub>-N) and nitrate (NO<sub>3</sub><sup>-</sup>-N) were determined in water samples in the Haihe River Basin. Furthermore, human health risk by water consumption were also assessed, it was obviously distributed with regional characteristics. For carcinogenic risk, there was Cd that were all under the  $5.0 \times 10^{5} a^{-1}$  in the whole basin, therefore, Cd was not a carcinogenic risk source of Haihe River Basin, in addition to this, the carcinogenic risk of Cr<sup>6+</sup> were larger than  $5.0 \times 10^{5} a^{-1}$  in six sites, especially the carcinogenic risk of Cr<sup>6+</sup> was almost 20 times larger than  $5.0 \times 10^{5} a^{-1}$  in the Aixinzhuang village of Xingtai City of Hebei Province, the concentration of Cr<sup>6+</sup> of Yongdinghe River system and estuary of Haihe river were all considerable higher than the acceptable level of  $5.0 \times 10^{5} a^{-1}$  in the whole river basin, besides that, the spatial distribution characteristics of As was similar with that of Cr<sup>6+</sup> in the Haihe River Basin, Furthermore, for the non-carcinogenic risk, the risk of non-carcinogenic risk of Pb, Hg, Cu, Zn, NH<sub>3</sub>-N and NO<sub>3</sub>-N are all less than  $5.0 \times 10^{5} a^{-1}$ , therefore, the potential human heath impact of water consumption were Cr<sup>6+</sup> and Cd, the pollution level need to be controlled in the future.

**Keywords:** Heavy metal pollution; Haihe river basin; Water environment; Health risk assessment

## Introduction

Heavy metals are ubiquitous in the environment [1,2]. It is natural situation that small amount of heavy metals existed in water, soil and food. Some kinds of elements of heavy metal such as manganese (Mn) copper (Cu) and zinc (Zn) are even essential for human body as structural and catalytic components of the enzyme [3]. However, most heavy metals are poisonous substances of natural human metabolism, As, Cd, Pb and Hg are endocrine-disrupting chemicals and affect the central nervous system [4,5].

If the amount of either kind of heavy metal in the environmental is larger than the certain threshold, serious health risk would be imposed to human health [1,3]. Addition to this, the water body that contain heavy metals will impose serious hazards to human health through human exposure by food consumption and dermal contact [6,7]. Health risk assessment has been developed widely since 1980s, it establishes the correlation of environmental pollution and human health risk as well as indicate and estimate qualitatively the potential hazardous probability that environmental pollution imposes to human health [8,6].

At present, the human health risk assessment methods of heavy metals were mainly based on the health risk assessment model of National Academy Society (NAS, 1983) and the United States Environmental Protection (USEPA, 1989). The method includes four processes, firstly hazardous identification, secondly evaluation of doseresponse relationship, thirdly evaluation of exposure extent and finally comprehensive health risk assessment.

This study aimed to identify the heath risk imposed by heavy metals pollution of the main streams in the Haihe River Basin, the conclusion can be used to help the water resource management bureau improve the general quality of water environment of Haihe river basin.

### Materials and Methods

### Study area and sampling

Study area: As was shown in Figure 1 Haihe river basin which

was one of the seven main river basins of China and located at North China and face to the Bohai Sea, the total area of the Haihe River basin was 31.82 km<sup>2</sup> and account for 3.3 percent of the total area of China. It contained three main river systems, Haihe river system, Luanhe river system and Tuhaimajiahe river system, as well as 7 main river systems. There was a high population density and many large and middle-medium scale cities were located in the area, such as Beijing, Tianjin. In addition to, it plays an important role in the political as well as economic activities. As a seriously degraded basin that interfered by human activities, water environmental problems of Haihe River Basin was very complex and the ecological risk level as well as the health risk level were high due to serious human interference. The comprehensive ecological integrity level and health level were needed to be improved in the future.

**Sampling collection:** From June to July of 2010, comprehensive field investigation was conducted on the mainstream of the Haihe River Basin and 44 water samples of the 7 main river systems were collected in order to discover the spatial distribution characteristics of the health risk level by heavy metals pollution of water environment.

### Analytical procedures

The concentration of As and Hg was analyzed by the Rayleigh Analytical Instrument (AF-610A) as well as the concentration of Cd was analyzed by ICP-MS,(VG-Q3, British). To protect the accuracy and the validity of the data, the standard materials provided by the National

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Standard Materials Center were also analyzed by the above instruments as it was lower than 10 percent therefore, the RSD (Relative Standard Deviation) data was validated.

### Health risk assessment model

Health risk assessment model were mainly based on the model of National Academy Society (NAS, 1983) and the United States Environmental Protection (USEPA, 1989). There were two hazardous substances to human health in water environment one was carcinogens, the other was non-carcinogens, and it was believed that intake heavy metals that contained in the drinking water was an important exposure approach.

## The health risk assessment model of genomic substances:

$$R^{C} = \sum_{i=1}^{K} R_{i}^{C}$$
$$R_{i}^{C} = \left[1 - \exp(-D_{i}q_{i})\right] (70a)^{-1}$$

Where  $R_i^C$  is average carcinogenic risk every person per year of genomic substances intake by water consumption approach,  $a^{-1}$  and  $D_i$  is the average daily exposure dose per body weight of genomic substances intake by water consumption approach,  $mg \cdot (Kg \cdot d)^{-1}$ , as well as  $q_i$  is the carcinogenic efficient of genomic substances intake by water consumption approach,  $mg \cdot (Kg \cdot d)^{-1}$ , the natural life of the human body is estimated as 70 years. If the heavy metals were intaken by drinking water the average daily exposure dose per human body weight ( $mg \cdot (Kg \cdot d)^{-1}$ ) can be estimated by following formula:

$$D_i = 2.2 L \times C_i \bullet (70 Kg)^{-1}$$

Where 2.2L is average daily drinking water volume that a junior person consume,  $C_i$  is the concentration of genomic poisonous substances in water body,  $(mg \bullet L^{-1})$ , the natural average body weight of a junior person is 70Kg.

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The health risk assessment model of non-carcinogens: For human body, most heavy metals besides of the Cr<sup>6+</sup>, Cd and As are non-carcinogens, the health risk imposed by non-carcinogens which contained in the drinking water can be estimated by the model:

$$R_i^n = \left(\frac{D_i}{D_{iRf}}\right) \times 10^{-6} \bullet \left(70a\right)^{-1},$$

Where  $R_i^n$  is average non carcinogenic risk every person per year of non-carcinogens intake by water consumption approach,  $a^{-1} D_i$  is the average daily exposure dose per body weight of non-carcinogens intake by water consumption approach,  $mg \cdot (Kg \cdot d)^{-1}$ ,  $D_{iRf}$  is the critical comparison dose imposed by non-carcinogens substances intake by water consumption approach,  $mg \cdot (Kg \cdot d)^{-1}$ , the natural life of the human body is estimated as 70 years. Addition to this, it was supposed that the total health risk that imposed by the whole heavy metals intake by water consumption can be estimated by counting up that of single heavy metal. Therefore, the total health risk intake by

water consumption is:  $R_s = R_i^C + R_i^n$ .

Setting of the health risk assessment standard: The carcinogenic intensity coefficient (Table 1) and noncarcinogenic intensity coefficient (Table 2) are most important parameters in the health risk, it can be calculated based on the classification standard of International Agency for Research On Cancer (IARC) and World Health Organization (WHO). Furthermore, the maximum risk acceptable level can be estimated as  $5 \times 10^{-5} \cdot a^{-1}$  based on the Superfund Public Health Evaluation Manual (USEPA, 1986).

### **Conclusion and Discussion**

## Non-carcinogenic risk of Haihe River Basin

The results of current study shows that the noncarcinogenic risk of Pb, Hg, Cu, Zn, NH<sub>3</sub>-N and NO<sub>3</sub><sup>-</sup>-N are all less than  $5.0 \times 10^{-5} \cdot a^{-1}$  which was the maximum acceptable risk level of USEPA, they all range from  $10^{-11}$  to  $10^{-8}$ , as well as the maximum noncarcinogenic risk of all study sites was estuary of Duliujian River in which noncarcinogenic risk of Hg was  $1.65 \times 10^{-8}$ , because most concentration levels of Pb and Hg were

Carcinogenic substances	$D_i / mg \bullet (Kg \bullet d)^{-1}$
Cd	6.1
As	15
Cr <sup>6+</sup>	41

Table 1: Coefficient of carcinogenic intensity.

Non-carcinogens	$D_i / mg \bullet (Kg \bullet d)^{-1}$
Pb	1.4 <sub>×10-3</sub>
Hg	3.0 <sub>×10<sup>-4</sup></sub>
Cu	4.0×10-2
Zn	3.0 <sub>×10-1</sub>
NH <sub>3</sub> -N	9.7 <sub>×10<sup>-1</sup></sub>
NO <sub>3</sub> -N	1.6

Table 2: Coefficient of noncarcinogenic intensity.

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under the detection limits (0.005 ug/mL and 0.004 ug/mL respectively), noncarcinogenic risk level of them were not calculated. Heavy metal pollution of Pb and Hg were controlled effectively after many water pollution tactics were conducted. According to Li and Liu [6], the noncarcinogenic risk order of Pb, Hg and Cu of Luan He River Basin which was a tributary of Haihe River Basin was Pb>Hg>Cu.

As was showed in (Figure 2), the carcinogenic risk of all study sites were ranged from  $10^{-4} \sim 10^{-7}/a^{-1}$ , and the carcinogenic risk of Cd were all under the  $5.0 \times 10^{-5} \cdot a^{-1}$  in the whole basin. Therefore, Cd was not a carcinogenic risk source of Haihe River Basin. Besides, the carcinogenic risk of Cr<sup>6+</sup> was almost 20 times larger than  $5.0 \times 10^{-5} \cdot a^{-1}$ in the Aixinzhuang village of Xingtai City of Hebei Province, the major industry of Xintai City was equipment manufacturing industry, coal & salt chemical industry and new typical architectural materials industry in which plenty of heavy metal materials were used in production,







furthermore, there were many sub-rivers influx at Aixinzhuang village and inflow in Fuyangxinhe River, so it was obviously the concentration of Cr<sup>6+</sup> which was the main pollutants of equipment manufacturing industry and was considerably high in the Aixinzhuang village.

Moreover, the concentration of Cr<sup>6+</sup> of Yongdinghe River system was also more higher than that of the whole river basin, it can be obviously deduced that the concentration of Cr6+ of Gudingqiao, upstream of Cetian reservoir and estuary of Haihe river were 1.44×10-<sup>4</sup> ug/mL, 2.97×10<sup>-4</sup> ug/mL and 1.49×10<sup>-4</sup> ug/mL respectively which were considered higher in the whole river basin. According to [9], Cr<sup>6+</sup> was the largest health risk source of carcinogens in Yanghe River and Sangganhe River, while the Sanganhe River is the downstream of Cetian reservoir, thus it was easy to deduce that carcinogenic risk of Cr<sup>6+</sup> was also higher in the Cetian reservoir as same as in the Yongdinghe River System. Cetian reservoir which was joined with Guanting reservoir by Sanggan River, and the Guanting reservoir was the second drinking water source and it was ceased to supply water for Beijing for serious water quality at 1997 [10]. The higher carcinogenic risk of Cr6+ in Cetian reservoir directly make the water quality recovery of Guanting reservoir a considerable difficult objective in the future. Furthermore, the carcinogenic risk of As of Haihe River Basin was obviously distributed with regional characteristics. It was higher than acceptable level of 5.0×10<sup>-5</sup>•a<sup>-1</sup> in Guding Bridige and Cetian Reservoir of Yongdinghe River System, in which the carcinogenic risk of As in Guding Bridge Upstream of Cetian Reservoir were about twentyfour times higher than the acceptable level of  $5.0 \times 10^{-5} \cdot a^{-1}$  respectively, addition to this, it was also higher than acceptable level of  $5.0 \times 10^{-5} \cdot a^{-1}$ in Xinji Dam of Zhanweinanhe River of Zhangweinan River System, as

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well as it were higher than acceptable level of  $5.0 \times 10^{-5} \cdot a^{-1}$  in Zhongbei Dam, Liaocheng City, Zhahe River Bridge of Majiahe River System and it were higher than acceptable level of  $5.0 \times 10^{-5} \cdot a^{-1}$  in Shen County and Yucheng of Tuhaihe River System in which the carcinogenic risk of Xinji Dam of Zhanweinanhe River was two times higher than acceptable level of  $5.0 \times 10^{-5} \cdot a^{-1}$  in Zhangweinan River System, besides that, the carcinogenic risk of Zhongbei Dam and Liaocheng City of Majiahe River System were three times and 1.4 times higher respectively than the acceptable level of  $5.0 \times 10^{-5} \cdot a^{-1}$ , addition to this, the carcinogenic risk of Shen County and Yucheng County were 1.6 times and 2.9 times higher than the acceptable level of  $5.0 \times 10^{-5} \cdot a^{-1}$ .

As was shown in (Figure 3), the comprehensive health risk level of Cr<sup>6+</sup>, As and Cd can be classified into four clusters, the first and the second clusters contained most sampling sites and the third cluster contained S34, Xinji Dam of Zhangwei nan river, S36, the Estuary of Zhangweinan river and S43, Zhangweinan river in the Yucheng County in which all belong to the Zhangweinan river system, the forth cluster contained S9, the Estuary of Haihe river, the fifth cluster contained S5, the Gudingqiao Bridge, S6 Upstream of Cetian Resvoir in which all belong to the Yongdinghe river system as well as the sixth cluster contained S23, Aixinzhuang village which belong to the Hutuohe river – Fuyanghe river - Ziyahe river system.

As it was shown in (Figure 4) the risk level of  $Cr^{6+}$  in the Haihe River Basin can be classified into three areas, the first area was light carcinogenic risk area in the Haihe River Basin, most sampling sites were contained in the area, that is to say the carcinogenic risk of  $Cr^{6+}$  of most river systems in the Haihe River Basin were light, the second area was moderate carcinogenic risk area in the Haihe River Basin and there





were four sampling sites, S5, S6, S9 and S15 located in the area, S5 was Guding Bridge, S6 was Upstream of Cetian Reservoir in which all were located in the upstream of the Sanganhe River, it was contaminated by the mining industry and Metal smelting industry of Shanxi Province as well as the concentration of  $Cr^{6+}$  was higher than the other river systems in the Haihe River Basin [9]. The third area was high carcinogenic risk of  $Cr^{6+}$  area in the Haihe River Basin, there were two sampling sites in the area, S15 Jinghai County and S23 Aixingzhuang village, where there were many small-scale factories in the Jinghai County and the Duliujianhe River was polluted seriously by them. Aixingzhuang village was located in the upstream of Fuyanghe River which was also polluted seriously and the water quality was inferior to fifth class for a long time. In Addition, there were many industries which produce high concentration of  $Cr^{6+}$ , thus the carcinogenic risk level was considerably higher in the area.

The cluster Analysis conclusion of health risk level of As in the Haihe River Basin can be seen in (Figure 5), there were four clusters in which the first cluster contained S5, Gudingqiao Bridge, S6, Sangganhe River Bridge which belong to the Yongdinghe River System, S34, Xinji Dam, S36, Zhongbei of Majiahe River which belong to the Majiahe River System, S43, Tuhaihe River of Yucheng County which belong to the Tuhaihe River System, as well as the second cluster contained S37, Majiahe River of Liaocheng City and S41, Tuhaihe River of Shenxian County, the third cluster contained S2 and S3 which belong

to the Luanhe River System, S8, Guanting Resvoir which belong to the Yongdinghe River System, the forth cluster contained S24, Ziyahe River on the Xian County which belong to the Hutuohe river– Fuyanghe river - Ziyahe river system, S32, Weihe River on the Guantao village as well as S35. Estuary of Zhanweinanhe River belong to the Zhangweinan River System.

As can be seen in (Figure 6), the carcinogenic health risk level of Cd in the Haihe River Basin by cluster analysis were attributed to two clusters, in addition to this, the Haihe River Basin can also be attributed into two areas according to the result of Cluster Analysis, the first area was light carcinogenic health risk level of Cd, there were S6, Up stream of Cetian Resvoir, S9, Estuary of the Haihe River and S17, Gangnan Resvoir in the area, according to the above results, the three sampling sites were contained in high carcinogenic risk of Cr<sup>6+</sup>, that is to say that the comprehensive carcinogenic risk of Cr6+ was light in the Haihe River Basin as well as the area where carcinogenic risk of Cr<sup>6+</sup> was high but the carcinogenic risk of Cd was not high respectively. The second area was moderate carcinogenic risk of Cd, there were also three sampling sites contained in the area, S7, Sangganhe River Bridge, S8, Upstream of Guanting Resvoir, S30, Zhangweinan River in the Weihui County where S7 and S8 belong to the Yongdinghe River System and S30 belong to the Zhangweinan River system which were all seriously polluted river systems in the Haihe River Basin.

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