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### **Potential risk assessment of heavy metal pollution in water from tributaries of Yinma River, Changchun, China**

This work shows human health risk assessment, ecological adverse risk and sources of heavy metals in water of Yinma River. Heavy metals as Copper and Zinc in 17 water samples were determined. The average concentration of Copper was lower, 0.0117 mg/L, while Zinc was higher, 0.0270 mg/L. To evaluate the potential risk or human health risk and ecology, risk quotient (RQ) and hazard quotient (HQ) were employed. The calculated RQs and the HQs for ingestion and dermal adsorption were all smaller than 1, indicating little or no adverse impact of the heavy metals exposure on human health and ecology. The results suggested that the sources of heavy metals in the river water were primarily from vehicular emission, burning biomass and coal.

**Key words:** Yinma River, heavy metals, human health risk assessment.

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#### **Инма өзенінің салалары суының ауыр металдармен ластануын әлеуетті бағалаудың қаупі (Чанчунь қ., Қытай)**

Аталған жұмыс адам денсаулығы үшін қаупін бағалау, экологиялық қаупін және Инма өзеніндегі судағы ауыр металдардың көздерін сипаттайды. 17 су сынамаларында мыс және мырыш сияқты ауыр металдар анықталды. Мыстың орташа концентрациясы 0,0117 мг/л төмен болды, ал мырыштың концентрациясы 0,0270 мг/л жоғары болды. Әлеуетті қауіпті немесе адам денсаулығы үшін қауіпті және экологияны бағалау үшін әлеуетті коэффициент (RQ) және қауіптілік факторы (HQ) пайдаланылды. Ішке қабылдау және адсорбция үшін есептелген RQs мен HQs шамалары анықталды, адам денсаулығы мен экология бойынша ауыр металдар әсері аз немесе жоқ қолайсыз әсер көрсетті, ол 1 төмен болды. Алынған нәтижелер өзенде негізінен ауыр металдардың көздері ретінде, биомасса мен көмір жағу, көлік құралдарының эмиссиясы екенін көрсетті.

**Түйін сөздер:** Инма өзені, ауыр металдар, адам денсаулығы үшін қаупін бағалау.

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#### **Потенциальная оценка риска загрязнения тяжелыми металлами вод из притоков реки Инма (г. Чанчунь, Китай)**

Данная работа представляет оценку риска для здоровья человека, экологический риск и источники тяжелых металлов в воде реки Инма. Были определены такие тяжелые металлы, как медь и цинк, в 17 пробах воды. Средняя концентрация меди была ниже 0,0117 мг/л, в то время как цинк был выше 0,0270 мг/л. Чтобы оценить потенциальный риск или риск для здоровья человека и экологии, были использованы параметры, как коэффициент риска (RQ) и фактор опасности (HQ). Вычисленные значения RQs и HQs для приема внутрь и кожной адсорбции были меньше 1, что указывает на практически наименьшее или полностью отсутствующее воздействие тяжелых металлов на здоровье человека и экологический статус района. Полученные результаты свидетельствуют о том, что источниками тяжелых металлов в речной воде были, прежде всего, автомобильные выхлопы, а также сжигание биомассы и угля.

**Ключевые слова:** река Инма, тяжелые металлы, оценка риска для здоровья человека.

## Introduction

In our days one of the actual problem of the world is environment pollution, specially water pollution, because water is essential source for human life and reason of pollution is human activity and development of industry. Usually industrial hubs locates near water objects and toxic substances immediately finds in river water. Consumption of this river water leads to degradation of health local population.

Jilin province of the Northeast region of China. It borders Russia to the east, North Korea to the southeast, the Chinese provinces of Liaoning to the south and Heilongjiang to the north, and the Inner Mongolia Autonomous Region to the west. The capital is Changchun, in the west-central part of the province. Area 72,200 square miles (187,000 square km). Population (2010) 27,462,297.

Jilin is a major producer of food crops, mainly rice, corn (maize), grain sorghum, millet, and beans. Most of the rice fields are in its eastern part, the Yianbian Korean Autonomous Prefecture being a noted rice-producing area of northern China. The most important commercial crops are sugar beets and tobacco, as well as flax, sunflower, and sesame.

Jilin is relatively highly industrialized and is a major producer of automobiles, chemicals, machine tools, power, and forest products. Originally a lumbering and food-processing centre, the province acquired a heavy industrial base during the Japanese occupation of 1931–45. It was a major beneficiary of Soviet investment in the mid-1950s, acquiring an automotive industry and metals and fabrication industries. Beginning in the 1960s the development of hydroelectric power in the province made possible the development of chemical and ferro-alloy industries. Most industry is concentrated in the two largest cities in the province – Changchun and Jilin.

Changchun is the capital and largest city of Jilin province, located in the northeast of the People's Republic of China, in the center of the Songliao Plain. It is administered as a sub-provincial city including counties and county-level cities, with a population of 7,677,089 at the 2010 census under its jurisdiction. The urban area had a population of 3.53 million people. The city's main urban area, including 5 districts and 4 development areas, had a population of 3,908,048 in 2010. The name, which means «Long Spring», originated from the Jurchen language. Known as China's Automobile City, Changchun is an important industrial base with a particular focus on the automotive sector. Apart

from this industrial aspect, Changchun is also one of four «National Garden Cities» awarded by the Ministry of Construction of P.R. China in 2001 due to its high urban greening rate.

The city's leading industries are production of automobiles, agricultural product processing, biopharmaceuticals, photo electronics, construction materials, and the energy industry. Changchun is the largest automobile manufacturing, research and development center in China, producing 9 percent of the country's automobiles in 2009. Changchun is home to China's biggest vehicle producer FAW (First Automotive Works) Group, which manufactured first Chinese truck and car since 1956. The automaker's factories and associated housing and services occupies a substantial portion of the city's southwest end. Specific brands produced in Changchun includes the Flag luxury brand, as well as joint ventures with Audi, Volkswagen, and Toyota. In 2012, FAW sold 2.65 million units of auto. The sales revenue of FAW amounted to RMB 408.46 billion, representing a rise of 10.8% on year. As cradle of the auto industry, one of Changchun's better known nicknames is «China's Detroit».

Yinma River is a tributary of the Songhua River second, full length 386.8 km, watershed area of 17400 km<sup>2</sup>, is located in the middle reaches of the second Songhua River basin. Yinma River originates in Panshi City of Jilin province Hulan Ling Zhen, Nong'an Country patron flow to inject second Songhua River. The main tributaries of Yinma River from upstream to downstream including: Shuangyang River, road river, small Nanhe, fog River, Yitong river. Among them, the largest tributary of the Yitong River Basin area accounted for half, a tributary of Xinkai River empties into the fog River; tributary dry fog Haihe import, distribution of water as shown in figure 1. The main stream of Yinma River in Panshi town above the chimney hilly area, shrubs, Kawa Tanihiro 1 km, I relatively flat, the two sides more paddy fields, river bend, a narrow and deep channel; Yan Tong Shan Zhen to Shitoukoumen Reservoir River, along the river is gentle hills and tableland; to Shitoukoumen Reservoir Dam to the estuary, coast are undulating plateaus and plains. Yinma river basin climate long cold winter, warm summer and rainy years, the average water temperature of 4.9 °C, average rainfall is 587 mm. the total amount of water resources in the basin is 2472000000 m<sup>3</sup>, the amount of water resources per capita as 378 m<sup>3</sup> is a national level 18%.

Yinma River basin range Changchun City, Jilin Province, the economy is the central area, in North-

east Black Soil Zone core area, is the main crop of corn, rice and other food of the province, is the north-east old industrial base and the country's main commodity grain base. Long term since the formation of walking with mechanical processing, processing of agricultural product paper for the leading industrial

structure. In 2011 the whole basin has a population of 8009000, the urbanization rate of 68.4%. Thus, Yinma River basin occupies an important position in the national economy of Jilin Province, has an important strategic status for spurring the rapid development of the province's economic and social.

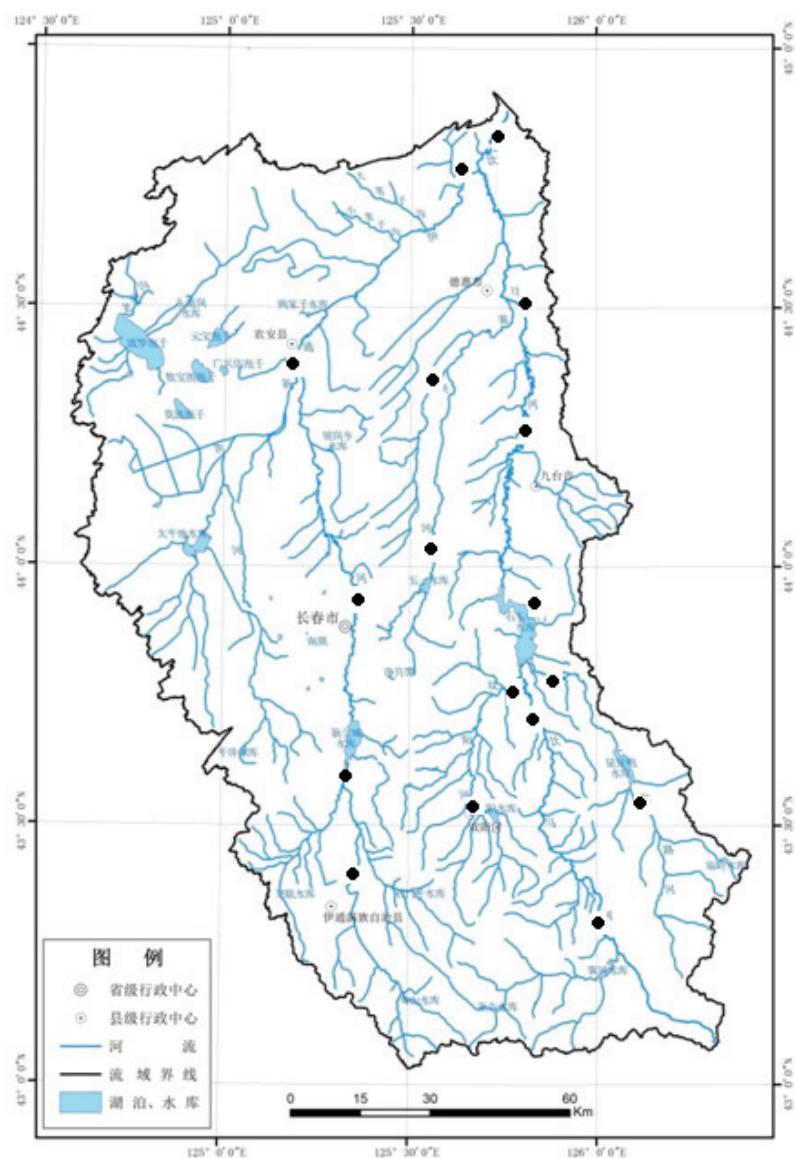


Figure 1 – The locations of sampling sites

## Materials and Methods

Water sampling was performed in October 2014 from tributaries of Yinma River, Changchun, China. A total of 17 water samples covered all the directions. The sampling locations are shown in figure 1,

2 liters of water was collected from each sampling site and transported to the laboratory to analyze. Temperature and pH were recorded in the field.

Heavy Metals analysis in the water samples

The water samples were filtered through 0.45- $\mu$ m glass fiber filter. The amount of heavy metals in water were determined with using Z-5000, zee-

man atomic absorption spectrophotometer, hitachi limited corporation (Graphite furnace).

The risk quotient (RQ) for each heavy metal can assess the potential human health ecological effects in the aquatic environment (Jiang et al. 2014). RQ was obtained by eq. 1:

$$RQ = \frac{\text{Monitoring concentration of } i}{\text{Allowable concentration of } i} \quad (1)$$

Where Allowable concentration of heavy metal used from USEPA (USEPA 2008)

The RQ can be more correctly assessed by follow methods:

$$RQ(wc) = \frac{\text{Maximum monitoring concentration of } i}{(\text{Allowable concentration of } i)} \quad (2)$$

$$RQ(bc) = \frac{\text{Minimum monitoring concentration of } i}{(\text{Allowable concentration of } i)} \quad (3)$$

Where RQ(wc) and RQ(bc) risk quotient in worst and best cases respectively. RQ(bc) >1 or RQ(wc) <1 usually can independently judge the risk level (Jiang et al.2014; Houtman 2014).

Human health risk assessment is based on reliable exposure pathways of contaminants (USEPA 1989, 1997). Heavy metals in water exposed to human body mainly through the following pathways: 1) direct ingestion of water consumption, 2) dermal absorption of contaminants in water adhered to exposed skin.

The expose doses through ingestion and dermal absorption pathway were calculated by use of eq.4 and eq.5 respectively, which were adapted from US Environmental Protection Agency (USEPA 1989):

$$D_I = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (4)$$

$$D_d = \frac{C \times SA \times K_p \times ET \times EF \times ED \times CF}{BW \times AT} \quad (5)$$

Where  $D_I$  daily intake of pollutant (mg/kg-d);  $D_d$  daily intake through dermal absorption (mg/kg-d);  $C$  concentration of pollutant in an environmental medium (e.g., mg/kg for soil or food, mg/L for water, mg/m<sup>3</sup> for air);  $IR$  intake rate of the environmental medium 1.41 L/day (USEPA 1997) (e.g., kg/day for food or soil, L/day for water, m<sup>3</sup>/day for air);  $BW$  body weight (kg) in this study 53.6 kg (MHPRC 2007);  $EF$  exposure frequency (days/yr) in this study 365 days/yr;  $ED$  exposure duration (years) 73.65 years (MHPRC 2007);  $AT$  averaging time (days) for non-carcinogens and carcinogens  $ED \times 365$  days;  $SA$  (cm<sup>2</sup>) surface area 20091 cm<sup>2</sup>;  $K_p$

(cm/h) dermal permeability coefficient;  $ET$  (h/day) exposure time during bathing and shower 0.3 h/day;  $CF$  unit conversion factor (USEPA 1989) L/1000 cm. The variables of  $IR$ ,  $EF$ ,  $ED$ ,  $SA$ ,  $BW$  and  $ET$  were collected from the USEPA and Ministry of Health of the People's Republic of China (MHPRC 2007), parameters are shown in tab.1.

**Table 1** – The random variables in HQ assessment

Definition	Units	Values
Ingestion rate (IR) <sup>a</sup>	L/day	1.41
Exposure frequency (EF) <sup>b</sup>	day/year	365
Exposure duration (ED) <sup>c</sup>	year	73.65
Body weight (BW) <sup>c</sup>	kg	53.6
Surface area (SA) <sup>a</sup>	cm <sup>2</sup>	20091
Exposure time during bathing and shower (ET) <sup>c</sup>	min/day	20
Gastrointestinal absorption factor (ABSg) <sup>d</sup>	unitless	0.5

a (USEPA 1997)

b (USEPA 1989)

c (MHPRC 2007)

d (USERDC 2005)

The hazard quotient (HQ) was calculated by eq.6 to estimate non-carcinogenic risk (USEPA 1989):

$$HQ = D / RfD \quad (6)$$

Where  $D$  (mg/kg-d) daily intake of pollutant obtained from the eq.1 and eq.2;  $RfD$  the reference dose of a certain pollutant for non-carcinogenic risk (USEPA 2008). The dermal absorption reference doses  $RfD_d$  are calculated by eq.7:

$$RfD_d = RfD_i \times ABSg \quad (7)$$

Where  $ABSg$  is a factor of gastrointestinal absorption (USEPA 2004).

To assess the overall non-carcinogenic risk posed by all pollutants, the HQ calculated for each pollutant was summed and expressed as hazard index (HI) by the eq.8 (USEPA 1989);

$$HI = HQ_1 + HQ_2 + \dots + HQ_n \quad (8)$$

## Results and Discussion

Values of pollutants by analytical method shown in tab.2. The concentration of heavy metals varied



from 0.0017 mg/L and 0.059 mg/L. The mean values of Copper and Zinc are 0.0117 mg/L and 0.0270 mg/L respectively. Coefficients of variation Cv of Zinc is 56.9 % and of Copper is 50.9 %.

**Table 2** – The values of heavy metals in water samples

	Cu	Zn
Mean (mg/L)	0.0117	0.0270
Minimum (mg/L)	0.0017	0.0063
Maximum (mg/L)	0.0249	0.059
Cv%	50.9	56.9

The maximum concentration of Zinc was in sampling site # 11, the highest concentration of Copper was in sampling site # 2, which could be explained by agriculture and industrial plants. Any way, the highest concentration of heavy metals occurred in the river inflows.

Physicochemical parameters of water were recorded in the field, pH varied from 7 to 8.43, mean value is 7.66, noticeable neutral to slightly alkaline in the water. Surface water temperatures ranged significantly, from 14.2°C to 25.9 °C.

The parameters of Hazard Quotients listed in tab.3. The  $RQ_{Cu}$  was more than 1 and posed decently or caused risk to the human health and ecology. Also the  $RQ_{wc}$  in worst cases were more than 1, which shows in sampling sites the concentrations of those metals caused little harmful damage. Other values of RQs were smaller than 1 indicates that heavy metals posed a little or no risk to the human health and ecology. When the  $RQ_{wc}$  for certain pollutant  $<1$ , the adverse effects caused by the pollutant exposure is minimal; the  $RQ_{bc}$  for a certain pollutant  $>1$ , the adverse effects caused by the pollutant exposure may be severe. The methods of best case RQ and worst case RQ are more refined analysis for assessing the risk levels,  $RQ_{bc}>1$  or

$RQ_{wc}<1$  usually can independently judge the risk level (Jiang et al.2014; Houtman 2014).

**Table 3** – Hazard quotients for heavy metals

	Cu	Zn
RQ (mg/L)	1.17	0.54
$RQ_{wc}$ (mg/L)	2.49	1.18
$RQ_{bc}$ (mg/L)	0.17	0.13
Di(mg/kg-d)	0.000308	0.000710
Dd(mg/kg-d)	0.00000	0.00000
HQ	0.01435	0.00442
HI	0.01877	

#### Human health risk assessment

The values of HQ were smaller than 1, that indicates no significant adverse effects on human health, whereas  $HQ>1$  is considered that adverse effects may occur to human health (Buchhamer et al.2012).

Hazard index (HI) $<1$  is considered no significant adverse effects of complex pollutants on human health, if  $HI>1$  indicates that the complex pollutants may pose adverse effects. In this study  $HI<1$  that indicates the exposure of heavy metals complex doesn't pose dramatic adverse effects on local consumers.

#### Conclusion

Over all, RQs and the HQs for ingestion and dermal adsorption were all smaller than 1, indicating little or no adverse impact of the heavy metals exposure on human health and ecology. The results suggested that the sources of heavy metals in the river water were primarily from vehicular emission, burning biomass and coal. The concentration of heavy metals varied from 0.0017 mg/L and 0.059 mg/L. The mean values of Copper and Zinc are 0.0117 mg/L and 0.0270 mg/L respectively. Coefficients of variation Cv of Zinc is 56.9 % and of Copper is 50.9 %.

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