*Pol. J. Environ. Stud. Vol. 32, No. 4 (2023), 3309-3322*
DOI: *10.15244/pjoes/159051* ONLINE PUBLICATION DATE: 2023-05-18

*Original Research*

# Study on Risk Model of Heavy Metals and Risk Element Pollution in Surface Farmland Soil in Cold Black Soil Region of China – Qianjin Town as an Example

**Qifa Sun[1, 3, 5]*, Ke Yang[1, 4]**, Zhuoan Sun[2]***, Jianheng Wang[3], Weiguo Xing[1], Guojie Hao[1]**

[1]Harbin Natural Resources Comprehensive Investigation Center, CGS, Harbin 150081, P.R. China
[2]Shenyang Laboratory of National Gemstone Testing Center, Shenyang 110034, P.R. China
[3]Shenyang Center of Geological Survey, CGS, Shenyang 110034, P.R. China
[4]Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences, Langfang 065000, P.R. China
[5]Northeast Geologica S&T Innovation Center of China Geological Survey, Shenyang 110034, P.R. China

*Received: 27 November 2022*
*Accepted: 5 January 2023*

**Abstract**

In order to study the pollution, ecological risk and health risk of heavy metals and risk elements in the surface farmland of the cold black soil area in Northeast China, the main grain production area in China, based on the collection and analysis of samples in 2010 and 2021, the soil heavy metals and risk element in this area were assessed by using the method of Geo accumulation index (Igeo), potential ecological hazard index (RI) and health risk assessment (HRA) model. The results show that there are heavy metals and risk element pollution in the soil, which is accumulated year by year. The average contents of Hg, Cd, Cr, Ni, Pb, Zn, As and Cu in the soil in this area are higher than the background values of Qianjin town. The heavy metals and risk element in the black soil and farmland in the cold area are obviously affected by human activities. There are different degrees of regional variability, and the coefficient of variation of Hg is 79%; Some elements have ecological risk, and Hg and Cd are the main influencing elements of soil ecological risk in shallow farmland; Heavy metals and risk element have non-carcinogenic health risks to children. The carcinogenic risk index of adults and children exceeded the soil treatment benchmark value of $10^{-6}$ proposed by EPA, As is the element that contributes the most to non-carcinogenic health risk and carcinogenic health risk in adults and children. In view of the continuous accumulation of heavy metals and risk element in farmland soil, it is necessary to improve ideological understanding, improve laws and regulations, formulate norms

*e-mail: 152468435@qq.com
**e-mail:yangkejs@qq.com
***e-mail:1144746765@qq.com

and standards, develop methods and technologies, and scientifically prevent and control heavy metals and risk element pollution.

**Keywords**: cold black soil, heavy metal pollution, ecological risk, health risks, northeast China

## Introduction

Black soil is a unique treasure given by nature to mankind. It is a kind of soil with good properties and high fertility, which is very suitable for plant growth, and also the most fertile soil in the world. It is characterized by pure black, and can only be formed in the cold temperate zone where the summer is warm and humid and the winter is cold and dry. Therefore, it is also known as cold black soil. It is also known as leached black soil because its formation requires leaching [1]. There are only four large black soil areas in the world, namely, the Ukrainian Plain in Ukraine, the Mississippi Plain in the United States, the Northeast Plain in China, and the Pampas grassland from Argentina in South America to Uruguay. Among them, the Pampas grassland is a subtropical red-black soil. Black soil is known as "giant panda in cultivated land" (China's national treasure) due to its good properties, high fertility and suitability for farming [2]. The black soil region in Northeast China bears the great responsibility of ensuring national food security and protecting black soil arable land. Due to the lack of understanding of the theory of sustainable development of environment and resources in the past, the pursuit of grain production in the era of shortage economy, coupled with the poor basic conditions of agricultural production and the low level of new technology application in the black soil area, the black soil suffered heavy metal pollution and further affected the ecology and human health [3].

Heavy metal pollution mainly refers to heavy elements with significant biological toxicity such as mercury, cadmium, lead, chromium, copper, nickel, zinc and metalloid arsenic [4]. Although As is not a heavy metal, its behavior, source and harm are similar to those of heavy metals, so it is usually included in the category of heavy metals for discussion [5]. It is very difficult for heavy metals to be biodegraded, but on the contrary, they can be enriched thousands of times under the biological amplification of the food chain [6] and finally enter the human body [7]. Heavy metals can interact strongly with proteins and enzymes in the human body, making them inactive, and may also accumulate in some organs of the human body [8], causing chronic poisoning [9]. In recent years, scholars at home and abroad have conducted in-depth research on heavy metal pollution. De conti et al. [10] studied copper and zinc in the soil of Santa Maria in the south of Brazil with a history of pig manure application and plant cultivation in 2016, and believed that the application of pig manure for many years increased the concentration of copper and zinc in the surface soil and the concentration of copper in the deep soil; Olatunde et al. [11] studied the distribution and pollution degree of heavy metals in the soil around a large cement plant in Ibesai, Ogun State, Nigeria in 2020, and considered that a large amount of cadmium, chromium, nickel and lead pollution and potential ecological risks were observed in the soil around the cement plant; Heimann et al. [12] studied the current situation of agricultural soil nutrients and pollutants in the suburb of Beijing in 2015, and believed that veterinary antibiotics and heavy metals promoting growth in animal husbandry reached the farmland through the application of fertilizers. These studies show that heavy metal pollution of farmland soil is widespread in the world. With the joint efforts of scientists, we have a certain understanding of the sources of heavy metals in the soil. Black soil areas have similar sources of heavy metals, but there are few special studies on their ecological risks and health risks. In particular, the heavy metal pollution of black soil in cold regions, which are the main grain producing areas, needs special attention.

## Regional Overview

Qianjin Town, belonging to Hailun City, Suihua City, Heilongjiang Province, is located in the west of Hailun city. The town government is located in Tangguozheng Tun, Qianjin village, with a longitude of 125°10′06″~127°44′47″, and a latitude of 45°44′47″~47°44′47″. The land area is 194.5 km$^2$, of which the cultivated land area is 133.33 km$^2$ and the registered residence population is 33872. There are 15 administrative villages under its jurisdiction. The east of Qianjin town is a plain, the north is a plain low-lying land, the middle is a transition zone between mountains and plains, the south is a hilly area, and a small amount of low-lying land is near the Helun river. The highest peak in the territory is Tang Guozheng Tun, located in Qianjin village, 182 m above sea level; The lowest point, Nanmaotun, is located in Guangrong village, 89 m above sea level. Qianjin town has a cold temperate monsoon climate with four distinct seasons. The winter is cold and long, with northwest wind and dry climate. In summer, the south wind is blowing, the weather is humid and hot and rainy, and the climate is humid. It is windy in spring and easy to be dry; In autumn, the temperature difference between day and night is large and the temperature drops quickly. Hailun river is a tributary of Tongken river. It flows from east to west through Tongxin village and Guangrong village in Qianjin town. It is 16.5 kilometers long and has a water supply and drainage systems area of 96 square kilometers. The soil type of Qianjin town is mainly black soil, which is rich in humus. The humus content of the surface soil reaches 5-6%, and the thickness can reach 60-80 cm. It has a good granular structure and is one of the most fertile soils. It is one of the major grain producing areas in China. The grain crops are mainly soybeans and corn, and the cash crops are mainly potatoes, melons and vegetables, sugar beets, etc. the livestock industry mainly focuses on raising pigs, cattle and sheep.

## Materials and Methods

### Sample Collection and Testing

Based on the analysis of basic data such as land use map, soil type map and geological map in the study area, the sampling points are arranged in grid form by using ArcGIS 10.8 software. That is, one sampling unit is set every 0.65 km$^2$, and one sample is collected from each sampling unit. The sampling point is arranged near the center of the sampling unit to avoid human pollution as much as possible. About 1kg of 0-20 cm surface soil sample is collected within 100m of the sampling point by plum blossom sampling method and loaded into clean cloth bags (Fig. 1). After the original soil samples are naturally dried, they are crushed with a wooden mallet and then passed through a 10 mesh (2 mm) nylon screen. After discarding the plant debris, rock debris, primary mineral particles and other sundries in the samples, they are loaded into clean polyethylene sample bottles. A total of 351 soil analysis samples are obtained and sent to the laboratory of the halbin natural resources comprehensive survey center of China Geological Survey for analysis and testing. After grinding the pre analysis sample to a particle size of less than 200 mesh

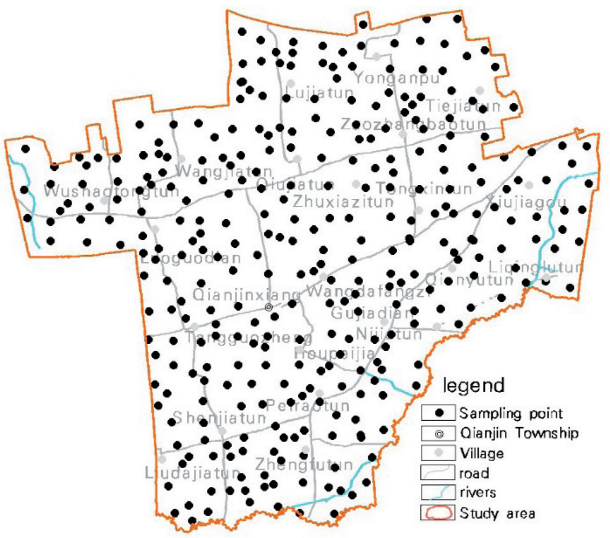


Fig. 1. Distribution map of sample collection points.

(0.075 mm), analyze the contents of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. Among them, Cr, Pb, Zn, Cu and Ni were determined by X-ray fluorescence spectrometer (PW4400/40). The detection limits were 2.79, 1.88, 1, 0.85 and 1.5 mg/kg respectively; Cd was determined by inductively coupled plasma mass spectrometer (I cap Qc) with a detection limit of 0.01mg/kg; As was determined by Atomic Fluorescence Photometer (XGY-2020) with a detection limit of 0.6 mg/kg; Hg was determined by cold atomic fluorescence spectrometer (XGY-1011a) with a detection limit of 0.005 mg/kg. According to the accuracy and precision of the national first-class soil reference materials (GBW Series), 5% of the samples were randomly selected for parallel testing. The qualified rate of the duplicate samples was 100%, and the data analysis quality met the relevant requirements.

## Evaluation Method

### Evaluation of Potentially Harmful Elements Pollution in Soil

The earth accumulation index method [13] is used to evaluate the pollution level of heavy metals in soil. The earth accumulation index method can reflect the natural change characteristics of the distribution of heavy metals, and can also judge the impact of human activities on the environment. It is an important parameter to distinguish the impact of human activities (Table 1). The calculation formula is:

$$I_{geo}=\log_2\left[\frac{C_i}{k\times S_i}\right] \quad (1)$$

Where $I_{geo}$ is the earth accumulation index; $C_i$ is the concentration of heavy metal i; $S_i$ Is the background value of the element; 1.5 is the background matrix correction factor [14].

Table 1. $I_{geo}$ index and the criteria of pollution grade.

| Index of geoaccumulation $I_{geo}$ | Level | Pollution degree |
|---|---|---|
| $I_{geo}$<0 | 0 | Pollution-free |
| 0≤$I_{geo}$<1 | 1 | Light pollution |
| 1≤$I_{geo}$<2 | 2 | Medium pollution |
| 2≤$I_{geo}$<3 | 3 | Medium to heavy pollution |
| 3≤$I_{geo}$<4 | 4 | Heavy pollution |
| 4≤$I_{geo}$<5 | 5 | Heavy to extremely heavy pollution |
| 5≤$I_{geo}$ | 6 | Extremely heavy pollution |

## Ecological Risk Assessment of Potentially Harmful Elements in Soil

The potential ecological hazard index method proposed by Swedish scientist Hakanson [15] was used. This is a method proposed from the sedimentological point of view according to the properties of heavy metals and environmental behavior characteristics to evaluate the pollution of heavy metals in soil or sediment. This method not only considers the content of heavy metals in the soil, but also comprehensively considers the multi-element synergy, toxicity level, pollution concentration and environmental sensitivity to heavy metal pollution, so it has been widely used in environmental risk assessment. The calculation formula is as follows:

$$RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} (T_r^i \times C_f^i) = \sum_{i=1}^{n} (T_r^i \times \frac{C_i}{C_n^i}) \quad (2)$$

Where, $C_f^i$ is the pollution index of a metal; $C_i$ is the concentration of a heavy metal in the soil; $C_n^i$ is the background value of a heavy metal; $E_r^i$ is the potential ecological risk index of a heavy metal; $T_r^i$ is the Toxicity Coefficient of a heavy metal. The toxicity coefficients of Zn, Cr, Cu, Ni, Pb, As, Cd and Hg are 1, 2, 5, 5, 10, 30 and 40 respectively [16]; RI is the total potential ecological risk index. According to $E_r^i$ and RI, single factor potential ecological hazards and total potential ecological hazards are classified (Table 2).

## Human Health Risk Assessment of Potentially Harmful Elements in Soil

The health risk of heavy metals depends on two aspects: one is the level of environmental pollution, including the concentration, form and toxicity of heavy metals. The second is human exposure behavior, including the behavior and characteristics of human exposure to heavy metals. After entering the soil, heavy metals enter the human body through skin contact, oral ingestion, and inhalation in the dust, which is harmful to human health. According to the health risk assessment model recommended by the United States Environmental Protection Agency [17], the harm (carcinogenic risk and non-carcinogenic risk) caused by heavy metal exposure in farmland soil in the study area is assessed and predicted. Because adults and children have different physiological characteristics and behavior patterns, different values are selected for parameters such as average body weight and exposure duration (Table 3).

The formula for calculating the daily average exposure of adults to heavy metals is:
Calculation of oral exposure:

$$ADD_{i\text{ing}} = \frac{C_i \times IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (3)$$

Calculation of exposure through respiratory route:

$$ADD_{i\text{inh}} = \frac{Ci \times InhR \times EF \times ED}{PEF \times BW \times AT} \quad (4)$$

Calculation of skin exposure:

$$ADD_{i\text{derm}} = \frac{C_i \times SA \times SL \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (5)$$

The formula for calculating the average daily exposure of children to heavy metals is:
Calculation of oral exposure:

$$LADD_{i\text{ing}} = \frac{C_i \times EF}{AT} \left( \frac{IngR_{child} \times ED_{child}}{BW_{child}} + \frac{IngR_{adult} \times ED_{adult}}{BW_{adult}} \right) \times 10^{-6} \quad (6)$$

Calculation of exposure through respiratory route:

$$LADD_{i\text{inh}} = \frac{C_i \times EF}{PEF \times AT} \times \left( \frac{InhR_{child} \times ED_{child}}{BW_{child}} + \frac{InhR_{adult} \times ED_{adult}}{BW_{adult}} \right) \quad (7)$$

Calculation of skin exposure:

$$LADD_{i\text{derm}} = \frac{Ci \times EF \times SL \times ABS}{AT} \times \left( \frac{SA_{child} \times ED_{child}}{BW_{child}} + \frac{SA_{adult} \times ED_{adult}}{BW_{adult}} \right) \times 10^{-6} \quad (8)$$

Various types of heavy metals will have different toxic effects after entering the human body through different exposure routes. The non-carcinogenic risk index HQ is used to assess the risk of non-cancer diseases caused by exposure to certain heavy metals, and the carcinogenic risk index Cr is used to assess the risk of cancer. The calculation formula is as follows:

$$HQ = \sum HQ_i = \sum \frac{ADD_{i\text{ing}} + ADD_{i\text{inh}} + ADD_{i\text{derm}}}{RfD_i} \quad (9)$$

Table 2. Indices used to assess the potential ecological risk status.

| Ecological hazards | Slight | Medium | Strong | Very strong | Extremely strong |
|---|---|---|---|---|---|
| Potential ecological hazard index of single potentially harmful elements $E_r^i$ | <40 | 40-80 | 80-160 | 160-320 | ≥320 |
| Total potential ecological hazard index *RI* | <150 | 150-300 | 300-600 | 600-1200 | ≥1200 |

$$CR = \sum CR_i = \sum \left( ADD_{i\text{ing}} + ADD_{i\text{inh}} + ADD_{i\text{derm}} \right) \times SF \quad (10)$$

The meanings of the symbols in the formula are shown in Table 4.

*RfD* and *SF* values of different exposure pathways are shown in Table 5 [20-22].

## Results and Discussion

### Distribution and Variation Characteristics of Heavy Metals in Soil

It can be seen from the characteristics of heavy metal content in the surface soil of the study area (Table 6) that the average values of the eight heavy

Table 3. Health risk exposure parameters of heavy metals.

| Symbol | Parameter | Unit | Adult reference value | Child reference value |
|---|---|---|---|---|
| ED | Exposure years | a | 25 | 6 |
| BW | Average weight | kg | 56.8 | 15.9 |
| EF | Exposure frequency | $d \cdot a^{-1}$ | 350 | 350 |
| AT | Average exposure time | d | Carcinogenic 26280, noncarcinogenic 9125 | Carcinogenic 26280, noncarcinogenic 2190 |
| IngR | Daily soil intake | $mg \cdot d^{-1}$ | 100 | 200 |
| InhR | Daily air respiration | $m^3 \cdot d^{-1}$ | 14.5 | 7.5 |
| SA | Exposed skin surface area | $cm^2$ | 2415 | 1295 |
| SL | Skin adhesion coefficient | $mg\ (cm^2 \cdot d)^{-1}$ | 0.2 | 0.2 |
| PEF | Surface dust emission factor | $m^3 \cdot kg^{-1}$ | $1.36 \times 10^9$ | $1.36 \times 10^9$ |
| ABS | Skin absorption factor | | 0.001 | 0.001 |

Note: the skin exposure area is calculated according to the exposed skin surface area of Chinese people and the climate characteristics of Qianjin town, and other parameters are calculated according to the human body parameters issued by the Ministry of environmental protection of China [18] and USEPA [19].

Table 4. Meanings of symbols in formula (9) and formula (10).

| Symbol | Parameter | Symbol | Parameter |
|---|---|---|---|
| *HQ* | Non-carcinogenic health risk index of all heavy metals | *CR* | Health risk index for carcinogenesis of all heavy metals |
| $HQ_i$ | Non-carcinogenic health risk index of single heavy metal i | $CR_i$ | Single heavy metal i carcinogenic health risk index |
| $RfD_i$ | Non-carcinogenic daily average intake of heavy metal I | *SF* | Carcinogenic slope factor |
| HQ or $HQ_i$<1 indicates that the non-carcinogenic risk of heavy metals is negligible, on the contrary, there is non-carcinogenic risk. | | $10^{-6} \sim 10^{-4}$ is the acceptable range of carcinogenic health risk index CR or $CR_i$. | |

Table 5. Reference calculated values and carcinogenic slope factors of different exposure routes of different heavy metals.

| Potentially harmful elements | Reference measurement RfD ($mg \cdot kg^{-1} \cdot d^{-1}$) | | | Carcinogen SF ($kg \cdot d \cdot mg^{-1}$) | | |
|---|---|---|---|---|---|---|
| | Through mouth | Skin | Breathing | Through mouth | Skin | Breathing |
| As | $3.0 \times 10^{-4}$ | $3.0 \times 10^{-4}$ | $1.5 \times 10^{-5}$ | 1.5 | 1.5 | $4.3 \times 10^{-3}$ |
| Cd | $1.0 \times 10^{-3}$ | $2.5 \times 10^{-5}$ | $1.0 \times 10^{-5}$ | 6.1 | 6.1 | 6.3 |
| Cr | $3.0 \times 10^{-3}$ | $7.5 \times 10^{-5}$ | $2.55 \times 10^{-5}$ | — | — | 42 |
| Cu | $4.0 \times 10^{-2}$ | $4.0 \times 10^{-2}$ | — | — | — | — |
| Hg | $3.0 \times 10^{-4}$ | $2.1 \times 10^{-5}$ | $3.0 \times 10^{-4}$ | — | — | — |
| Ni | $2.0 \times 10^{-2}$ | $8.0 \times 10^{-4}$ | $2.3 \times 10^{-5}$ | — | — | 0.84 |
| Pb | $3.5 \times 10^{-3}$ | $5.3 \times 10^{-4}$ | $3.5 \times 10^{-3}$ | — | — | — |
| Zn | $3.0 \times 10^{-1}$ | $3.0 \times 10^{-1}$ | — | — | — | — |

Table 6. Characteristic value of heavy metal content in surface soil.

| Characteristic parameter | Year | As | Cd | Cr | Cu | Hg | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| Minimum value | 2010 | 8.2 | 0.08 | 55.7 | 19.7 | 0.02 | 24.25 | 18.88 | 52.78 |
| | 2021 | 6.24 | 0.04 | 31.37 | 19.15 | 0.02 | 12.47 | 19 | 53.27 |
| Maximum value | 2010 | 12.8 | 0.17 | 73.9 | 27.7 | 0.04 | 33.5 | 27.2 | 79.9 |
| | 2021 | 14.84 | 0.47 | 84.38 | 86.85 | 0.51 | 36.68 | 79.22 | 154.33 |
| Average value | 2010 | 9.15 | 0.1 | 66.75 | 22.59 | 0.03 | 27.76 | 22.36 | 64.65 |
| | 2021 | 10.67 | 0.1 | 65.06 | 23.18 | 0.04 | 26.47 | 26.05 | 66.8 |
| Coefficient of variation (%) | 2010 | 8 | 17 | 6 | 5 | 14 | 7 | 6 | 8 |
| | 2021 | 9 | 30 | 7 | 17 | 79 | 7 | 15 | 11 |
| Hailun soil background value | | 9.14 | 0.07 | 42.46 | 17.78 | 0.03 | 23.65 | 20.23 | 52.05 |

Note: the background value of heavy metals in surface soil of Qianjin town is obtained from the statistics of China geochemical survey data [23]; The coefficient of variation is dimensionless.

metal contents in 2021 are higher than their background values, indicating that the heavy metals in the study area have accumulated in the soil to a certain extent. Among them, the accumulation degree of Cr is the highest, the content is between 31.37 and 84.38 mg/kg, the average value is 65.06 mg/kg, which is 1.53 times of the background value of Qianjin town; Cd, Zn, Hg, Ni, Pb, Cu and As are about 1.11~1.43 times of the background value of the soil in Qianjin town. The order of the elements is Cr>Cd>Hg>Cu>Pb>Zn>As >Ni. Compared with the data in 2010, the content of five elements (As, Cu, Hg, Pb, Zn) increased in 2021, of which Hg increased the most, 1.33 times as much as that in 2010; The content of two elements (Cr, Ni) decreased, 0.97 times and 0.95 times that of 2010, with little change; The content of one element (Cd) was the same as that in 2010. In general, the content of heavy metals in surface soil increased obviously under the influence of human activities.

From the perspective of the variability of heavy metal elements, the range of variation coefficient in 2010 is 5%~17%, and that in 2021 is 7%~79%, which is significantly higher than that in 2010. The variation coefficient of Hg is significantly higher than that of other elements, reaching 79%. Other elements have certain variability. The distribution of each element is shown in Fig. 2. The high value points of As are mainly distributed in Liuda Tun, Qianyu Tun and Li Qinglu Tun, the high value points of Cd are mainly distributed in Houpeijia Tun and Peiyao Tun, the high value points of Cr are mainly distributed in Zhaozhangbao Tun, Zhuxiazi Tun, Wang Yangtun and Luoguodian, the high value points of Cu are mainly distributed in Xiujiagou, and the high value points of Hg are mainly distributed in Li Qinglu Tun, the high value points of Ni are mainly distributed in Zhaozhangbaotun and Wangyangtun, the high value points of Pb are mainly distributed in Yong'anbao, and the high value points of Zn are mainly distributed in Yong'anbao.

## Analysis of Heavy Metal Pollution Degree

Through the evaluation of the accumulation index of the soil heavy metal pollution degree in Qianjin town (Table 7). It is concluded that the order of heavy metal pollution index in Qianjin town from high to low is Cr>Cd>Cu>Pb>Zn>As>Ni>Hg. From the mean value of pollution index, only Cr has light pollution, and other heavy metal elements have no pollution level. However, due to the different coefficient of variation of heavy metal elements, there are different levels of pollution of different elements in different regions. The pollution degree of soil Pb is the highest. There is one extremely heavy pollution point, one medium to heavy pollution point, one medium pollution point, and 13 light pollution points. The pollution points account for 4.56% of the total number of samples; The pollution coefficient of Cr is the largest, with 233 light pollution points, accounting for 66.38% of the total number of samples. Zn has heavy to extremely heavy pollution, Hg has heavy pollution, Cd has medium to heavy pollution, Cu has medium pollution, As and Ni have light pollution, of which Ni has only one light pollution point, which is basically in a pollution-free state.

## Potential Ecological Risk Assessment of Heavy Metals

According to the assessment of potential ecological hazard risk of soil in Qianjin town (Table 8), from the perspective of potential ecological risk of single heavy metal, the Hg hazard index ranges from 22.93 to 655.482, and there are slight, medium, strong, Very strong and extremely strong ecological risks, covering all ecological risk levels, mainly light and medium risks, accounting for 43.30%, medium risk accounting for 52.42%, strong risk accounting for 3.7%, very strong risk accounting for 0.28% and extremely strong risk accounting for 0.28%; The Cd risk index ranges

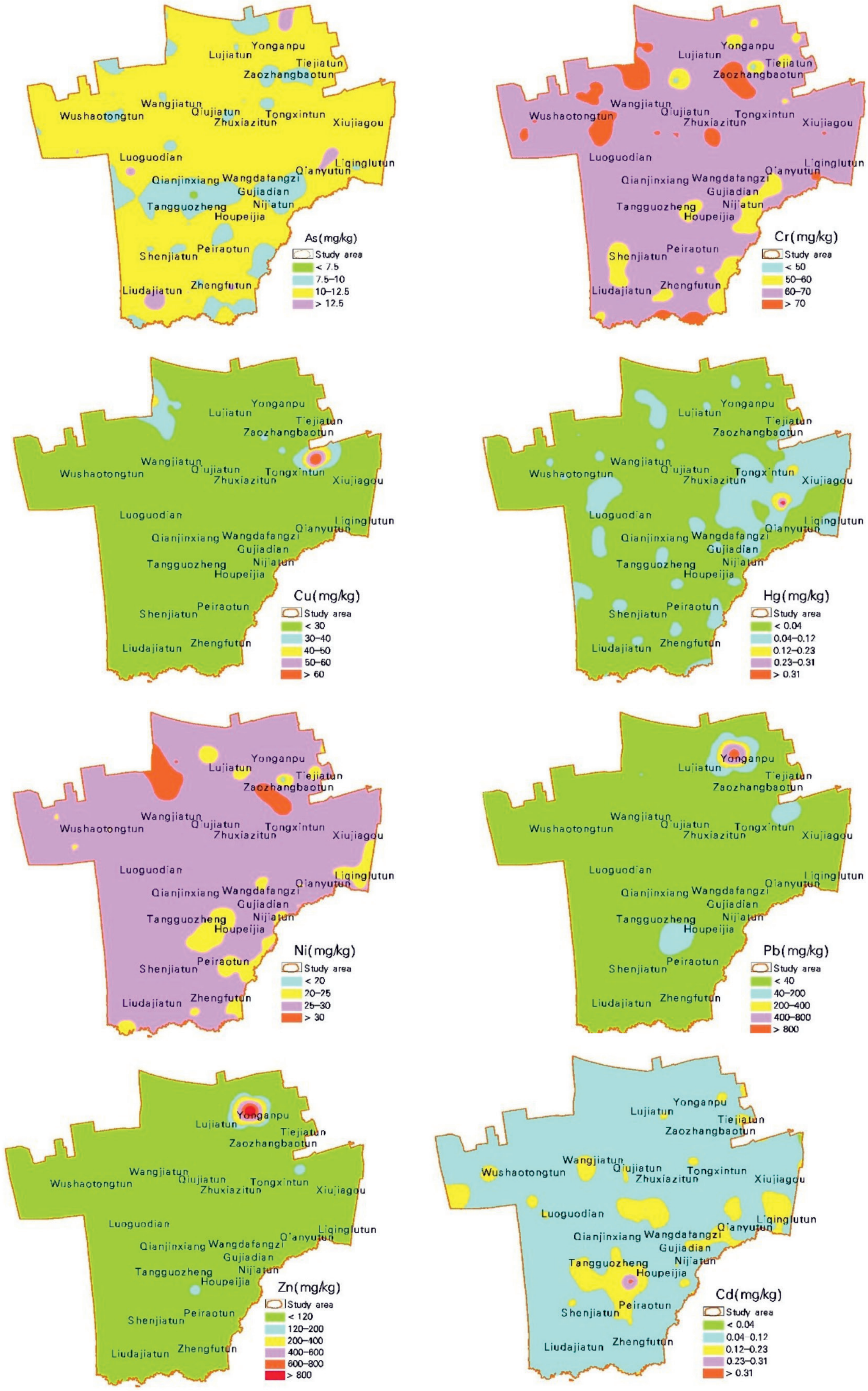


Fig. 2. Box plot of potentially harmful elements concentration.

Table 7. Classification of heavy metal pollution index of surface soil.

| Heavy metal | Index mean | Number of samples at all levels | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Pollution-free | Light pollution | Medium pollution | Medium to heavy pollution | Heavy pollution | Heavy to extremely heavy pollution | Extremely heavy pollution |
| Pb | -0.21 | 335 | 13 | 1 | 1 | 0 | 0 | 1 |
| Zn | -0.22 | 337 | 13 | 0 | 0 | 0 | 1 | 0 |
| Hg | -0.47 | 310 | 37 | 3 | 0 | 1 | 0 | 0 |
| Cd | -0.14 | 252 | 95 | 3 | 1 | 0 | 0 | 0 |
| Cu | -0.21 | 336 | 14 | 1 | 0 | 0 | 0 | 0 |
| Cr | 0.03 | 118 | 233 | 0 | 0 | 0 | 0 | 0 |
| As | -0.37 | 349 | 2 | 0 | 0 | 0 | 0 | 0 |
| Ni | -0.43 | 350 | 1 | 0 | 0 | 0 | 0 | 0 |

Table 8. Potential ecological hazard index of heavy metals in surface farmland soil.

| Hazard index | | Distribution range | Number of samples at all levels | | | | |
|---|---|---|---|---|---|---|---|
| | | | Slight | Medium | Strong | Very strong | Extremely strong |
| Ei | Hg | 22.93~655.482 | 152 | 184 | 13 | 1 | 1 |
| | Cd | 16.85~194.69 | 164 | 182 | 4 | 1 | 0 |
| | Pb | 4.70~312.08 | 350 | 0 | 0 | 1 | 0 |
| | Cr | 1.48~3.97 | 351 | 0 | 0 | 0 | 0 |
| | As | 6.83~16.23 | 351 | 0 | 0 | 0 | 0 |
| | Ni | 2.64~7.75 | 351 | 0 | 0 | 0 | 0 |
| | Zn | 1.02~24.44 | 351 | 0 | 0 | 0 | 0 |
| | Cu | 5.38~24.42 | 351 | 0 | 0 | 0 | 0 |
| RI | | 80.18~751.64 | 319 | 29 | 2 | 1 | 0 |

from 16.85 to 194.69. There are slight, medium, strong and very strong ecological risks, mainly slight and medium risks, with slight risks accounting for 46.72%, medium risks accounting for 51.85%, strong risks accounting for 1.14% and very strong risks accounting for 0.28%; The Pb risk index ranges from 4.70 to 312.08, with slight and strong ecological risks; Cr, As, Ni, Zn and Cu are all slight ecological risks; In general, Hg and Cd are the main elements of shallow soil ecological hazards.

From the perspective of the total potential ecological index RI, the distribution range of hazard index is 80.18~751.64, with slight, medium, strong and very strong ecological risks, accounting for 90.88%, 8.26%, 0.57% and 0.28% respectively, mainly minor ecological risks. The spatial distribution map of RI (Fig. 3) shows that the highest value of ecological risk occurs in Li Qinglu Tun, followed by Yong'anbao Tun. The impact factors are mainly Hg and Cd. The investigation found that agriculture and animal husbandry are the mainstay of the region, and animal husbandry is mainly for raising pigs, cattle and sheep. Pig, cattle and sheep dung are used as fertilizers in agriculture, causing heavy metal Hg and Cd pollution in the soil, increasing the ecological risk of the region.

## Human Health Risk Assessment

### *Assessment of Heavy Metal Exposure*

The assessment results of daily exposure to heavy metals in soil are shown in Table 9 and table 10. The average daily exposure to non-carcinogenic and carcinogenic substances by oral ingestion, skin contact and respiratory inhalation are in the following order: $ADD_{ing}$ > $ADD_{derm}$ >$ADD_{inh}$, mainly by oral ingestion, and far higher than the amount of heavy metals ingested in other ways. The average daily exposure of children to oral ingestion, skin contact and respiratory inhalation is higher than that of adults, the average daily exposure of non-carcinogenic elements and the average daily intake of different heavy metals are in the order of Zn>Cr> Pb>Ni>Cu>As>Cd>Hg. The average daily exposure of carcinogenic elements and the average

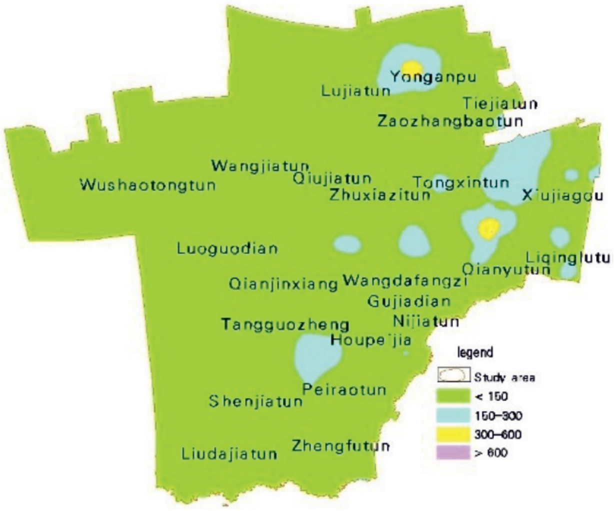


Fig. 3. Ecological risk zoning map of soil heavy metals.

daily intake of different heavy metals were in the order of Cr>Ni>As>Cd.

*Health Risk Assessment*

The evaluation results of non-carcinogenic health risk index of heavy metals are shown in Table 11.

It can be seen from the results in Table 11 that the non-carcinogenic risk of the same element through oral intake, skin contact and respiratory inhalation is $HQ_{ing}>HQ_{derm}>HQ_{inh}$, and oral intake is the main way of non-carcinogenic health risk of soil heavy metals. The non-carcinogenic health risks of different heavy metals are As>Cr>Pb>Ni>Cu>Zn>Hg>Cd. As is the most important influencing element of non-carcinogenic health risks. The average value of the impact index on adults and children is 6.05E-02 and 4.30E-01 respectively. The average value range of non-carcinogenic health risks of each element in adults is 2.10E-04~6.05E-02, the maximum value range is 9.63E-04~8.41E-02, and the average value of the total non-carcinogenic health risk index of each element is 1.24E-01, The maximum value is 7.89E-01; the average value of non-carcinogenic health risk of each element in children ranges from 1.31E-03 to 4.30E-01, and the maximum value ranges from 6.03E-03 to 5.98E-01. The average value of the total health risk index of each element is 8.39E-01, and the maximum value is 5.47E + 00, the average value and maximum value of single non-carcinogenic health risk index of heavy metals in adults and children are less than 1, indicating that there is no health risk of single heavy metals. The total health risk index of heavy metals in adults is less than 1, and the maximum value of the total

Table 9. Average daily non-carcinogenic exposure of heavy metals in soil (mg/(kg/d)).

| Heavy metal | Adult | | | | Children | | | |
|---|---|---|---|---|---|---|---|---|
| | $ADD_{ing}$ | $ADD_{inh}$ | $ADD_{derm}$ | $ADD$ | $ADD_{ing}$ | $ADD_{inh}$ | $ADD_{derm}$ | $ADD$ |
| Pb | 5.06E-05 | 5.39E-09 | 2.44E-07 | 5.08E-05 | 3.61E-04 | 9.96E-09 | 4.68E-07 | 3.62E-04 |
| Zn | 1.19E-04 | 1.27E-08 | 5.75E-07 | 1.20E-04 | 8.50E-04 | 2.34E-08 | 1.10E-06 | 8.51E-04 |
| Cr | 1.10E-04 | 1.17E-08 | 5.30E-07 | 1.10E-04 | 7.84E-04 | 2.16E-08 | 1.02E-06 | 7.85E-04 |
| Cd | 1.74E-07 | 1.86E-11 | 8.41E-10 | 1.75E-07 | 1.24E-06 | 3.43E-11 | 1.61E-09 | 1.25E-06 |
| Ni | 4.47E-05 | 4.76E-09 | 2.16E-07 | 4.49E-05 | 3.19E-04 | 8.80E-09 | 4.13E-07 | 3.20E-04 |
| As | 1.80E-05 | 1.92E-09 | 8.70E-08 | 1.81E-05 | 1.29E-04 | 3.55E-09 | 1.67E-07 | 1.29E-04 |
| Hg | 6.16E-08 | 6.56E-12 | 2.97E-10 | 6.19E-08 | 4.40E-07 | 1.21E-11 | 5.69E-10 | 4.40E-07 |
| Cu | 3.92E-05 | 4.17E-09 | 1.89E-07 | 3.93E-05 | 2.80E-04 | 7.71E-09 | 3.62E-07 | 2.80E-04 |
| ADD | 3.81E-04 | 4.07E-08 | 1.84E-06 | 3.83E-04 | 2.72E-03 | 7.51E-08 | 3.53E-06 | 2.73E-03 |

Table 10. Average daily exposure to carcinogenic heavy metals in soil (mg/(kg/d)).

| Heavy metal | Adult | | | | Children | | | |
|---|---|---|---|---|---|---|---|---|
| | $ADD_{ing}$ | $ADD_{inh}$ | $ADD_{derm}$ | $ADD$ | $ADD_{ing}$ | $ADD_{inh}$ | $ADD_{derm}$ | $ADD$ |
| Cr | 3.81E-05 | 4.06E-09 | 1.84E-07 | 3.83E-05 | 1.03E-04 | 5.86E-09 | 2.69E-07 | 1.04E-04 |
| Cd | 6.05E-08 | 6.45E-12 | 2.92E-10 | 6.08E-08 | 1.64E-07 | 9.31E-12 | 4.26E-10 | 1.65E-07 |
| Ni | 1.55E-05 | 1.65E-09 | 7.49E-08 | 1.56E-05 | 4.21E-05 | 2.39E-09 | 1.09E-07 | 4.22E-05 |
| As | 6.25E-06 | 6.67E-10 | 3.02E-08 | 6.29E-06 | 1.70E-05 | 9.63E-10 | 4.41E-08 | 1.70E-05 |
| ADD | 5.99E-05 | 6.39E-09 | 2.89E-07 | 6.02E-05 | 1.63E-04 | 9.22E-09 | 4.22E-07 | 1.63E-04 |

Table 11. Non-carcinogenic health risk index of soil heavy metals.

| Heavy metal | | Adult | | | | Children | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $HQ$ | $HQ_{ing}$ | $HQ_{inh}$ | $HQ_{derm}$ | $HQ$ | $HQ_{ing}$ | $HQ_{inh}$ | $HQ_{derm}$ |
| Pb | Max | 6.29E-01 | 6.09E-01 | 6.49E-05 | 1.94E-02 | 4.39E+00 | 4.35E+00 | 1.20E-04 | 3.72E-02 |
| | AVG | 1.49E-02 | 1.44E-02 | 1.54E-06 | 4.61E-04 | 1.04E-01 | 1.03E-01 | 2.85E-06 | 8.83E-04 |
| Zn | Max | 7.19E-03 | 7.16E-03 | | 3.46E-05 | 5.12E-02 | 5.11E-02 | | 6.62E-05 |
| | AVG | 3.98E-04 | 3.97E-04 | | 1.92E-06 | 2.84E-03 | 2.83E-03 | | 3.67E-06 |
| Cr | Max | 5.73E-02 | 4.75E-02 | 5.96E-04 | 9.17E-03 | 3.58E-01 | 3.39E-01 | 1.10E-03 | 1.76E-02 |
| | AVG | 4.41E-02 | 3.66E-02 | 4.59E-04 | 7.07E-03 | 2.76E-01 | 2.61E-01 | 8.48E-04 | 1.35E-02 |
| Cd | Max | 9.63E-04 | 8.00E-04 | 8.53E-06 | 1.55E-04 | 6.03E-03 | 5.71E-03 | 1.58E-05 | 2.96E-04 |
| | AVG | 2.10E-04 | 1.74E-04 | 1.86E-06 | 3.36E-05 | 1.31E-03 | 1.24E-03 | 3.43E-06 | 6.45E-05 |
| Ni | Max | 3.76E-03 | 3.10E-03 | 2.87E-04 | 3.74E-04 | 2.34E-02 | 2.21E-02 | 5.30E-04 | 7.16E-04 |
| | AVG | 2.71E-03 | 2.23E-03 | 2.07E-04 | 2.70E-04 | 1.69E-02 | 1.60E-02 | 3.83E-04 | 5.17E-04 |
| As | Max | 8.41E-02 | 8.35E-02 | 1.78E-04 | 4.03E-04 | 5.98E-01 | 5.97E-01 | 3.29E-04 | 7.73E-04 |
| | AVG | 6.05E-02 | 6.00E-02 | 1.28E-04 | 2.90E-04 | 4.30E-01 | 4.29E-01 | 2.37E-04 | 5.56E-04 |
| Hg | Max | 3.06E-03 | 2.86E-03 | 3.05E-07 | 1.97E-04 | 2.08E-02 | 2.04E-02 | 5.63E-07 | 3.78E-04 |
| | AVG | 2.19E-04 | 2.05E-04 | 2.19E-08 | 1.42E-05 | 1.49E-03 | 1.47E-03 | 4.04E-08 | 2.71E-05 |
| Cu | Max | 3.68E-03 | 3.67E-03 | | 1.77E-05 | 2.62E-02 | 2.62E-02 | | 3.39E-05 |
| | AVG | 9.84E-04 | 9.79E-04 | | 4.73E-06 | 7.00E-03 | 6.99E-03 | | 9.06E-06 |
| $HQ$ | Max | 7.89E-01 | 7.58E-01 | 1.13E-03 | 2.98E-02 | 5.47E+00 | 5.41E+00 | 2.10E-03 | 5.70E-02 |
| | AVG | 1.24E-01 | 1.15E-01 | 7.97E-04 | 8.14E-03 | 8.39E-01 | 8.22E-01 | 1.47E-03 | 1.56E-02 |

Note: Max-maximum value, AVG-average value.

health risk index of heavy metals in children is greater than 1, it shows that there is no non-carcinogenic risk of heavy metals to the health of adults, but there is non-carcinogenic risk to children, and prevention should be strengthened (Fig. 4).

The evaluation results of carcinogenic health risk index of heavy metals are shown in Table 12.

It can be seen from the results in Table 12 that the carcinogenic risk of the same element through oral intake, skin contact and respiratory inhalation is $CR_{ing}$>$CR_{derm}$>$CR_{inh}$, and oral intake is the main way of carcinogenic health risk for adults and children. The carcinogenic risk of each element is As>Cd> Cr>Ni, As is the element with the greatest impact on cancer risk (Fig. 5), and the average impact index on adults and children reached 9.43E-06 and 2.55E-05, respectively. The average value range of the influence of each element on adult carcinogenic risk is 1.39E-09~9.43E-06, the maximum value range is 1.93E-09~1.31E-05, the average value of adult carcinogenic risk total index is 9.97E-06, the maximum value is 1.50E-05, the average value range of the influence of each element on child carcinogenic risk is 2.00E-09~2.55E-05, the maximum value range is 2.78E-09~3.55E-05, the

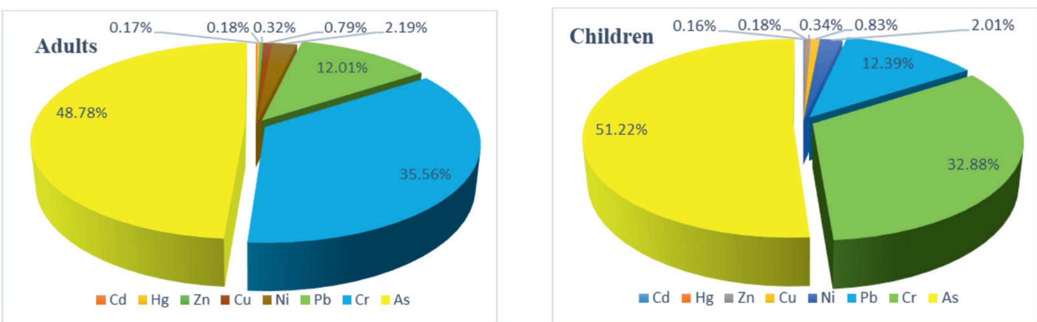


Fig. 4. HQ contribution rate of 8 heavy metals in soil of adults and children.

Table 12. Health risk index of soil heavy metal carcinogenesis.

| Heavy metal | | Adult | | | | Children | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $CR$ | $CR_{ing}$ | $CR_{inh}$ | $CR_{derm}$ | $CR$ | $CR_{ing}$ | $CR_{inh}$ | $CR_{derm}$ |
| Cr | Max | 2.21E-07 | | 2.21E-07 | | 3.20E-07 | | 3.20E-07 | |
| | AVG | 1.71E-07 | | 1.71E-07 | | 2.46E-07 | | 2.46E-07 | |
| Cd | Max | 1.70E-06 | 1.69E-06 | 1.87E-10 | 8.18E-09 | 4.61E-06 | 4.60E-06 | 2.69E-10 | 1.19E-08 |
| | AVG | 3.71E-07 | 3.69E-07 | 4.06E-11 | 1.78E-09 | 1.00E-06 | 1.00E-06 | 5.86E-11 | 2.60E-09 |
| Ni | Max | 1.93E-09 | | 1.93E-09 | | 2.78E-09 | | 2.78E-09 | |
| | AVG | 1.39E-09 | | 1.39E-09 | | 2.00E-09 | | 2.00E-09 | |
| As | Max | 1.31E-05 | 1.30E-05 | 3.99E-12 | 6.30E-08 | 3.55E-05 | 3.54E-05 | 5.76E-12 | 9.20E-08 |
| | AVG | 9.43E-06 | 9.38E-06 | 2.87E-12 | 4.53E-08 | 2.55E-05 | 2.55E-05 | 4.14E-12 | 6.61E-08 |
| CR | Max | 1.50E-05 | 1.47E-05 | 2.24E-07 | 7.12E-08 | 4.04E-05 | 4.00E-05 | 3.23E-07 | 1.04E-07 |
| | AVG | 9.97E-06 | 9.75E-06 | 1.72E-07 | 4.71E-08 | 2.68E-05 | 2.65E-05 | 2.48E-07 | 6.87E-08 |

Note: Max-maximum value, AVG-average value.

average value of child carcinogenic risk total index is 2.68E-05, and the maximum value is 4.04E-05, The carcinogenic risk index of all elements is less than $10^{-4}$, and the carcinogenic risk caused by heavy metals in the soil of Qianjin town is within the acceptable range. However, the carcinogenic risk index of adults and children exceeds the soil treatment benchmark value of $10^{-6}$ proposed by the United States EPA. Therefore, prevention should be strengthened.

## Discussion

With the rapid development of rural industrialization in China, the farmland soil in some areas has been polluted by heavy metals to varying degrees [24]. The content of heavy metals in the soil of Qianjin town has accumulated to a certain extent, which is greater than that in 2010 and more than that in 2008. In 2008, the soil Cd content was still lower than the background value, which was higher than the soil background value in 2010 and more obvious in 2021.

The spatial variation of heavy metals is significant, and the spatial distribution of different heavy metal elements is also different. The variation coefficient of Hg reaches 79%, which is consistent with the research of Song Hengfei [25]. The main factors affecting the accumulation of heavy metals in soil are the excessive use of chemical fertilizers, a large number of fungicides, lagging standards and regulations, low monitoring and management efficiency, and weak environmental awareness [26].

Ecological risk refers to the possibility that the ecosystem is affected by all elements outside the ecosystem that pose a threat to the ecosystem. The results of these effects may lead to damage to the structure and function of the ecosystem, thus endangering the safety and health of the ecosystem. Hg and Cd are the main influencing elements of shallow soil ecological hazards in the study area. The ecological hazard index of Hg is the highest, with an index range of 22.93~655.482, with slight, medium, strong, very strong and extremely strong ecological risks, followed by Cd with strong ecological risks. In the ecological

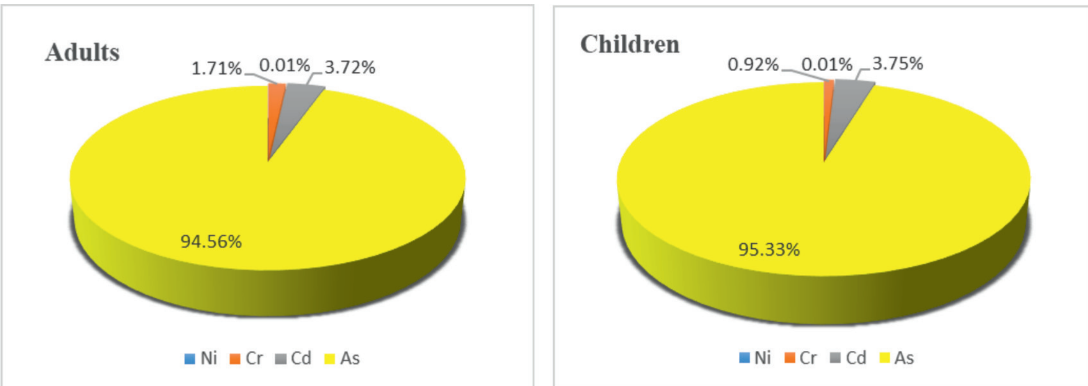


Fig. 5. Comparison of CR of four carcinogenic heavy metals in adults and children.

assessment of soil heavy metals in Ramsar region of Assam state, India, China's neighboring country, it is found that Zn and Mn have low ecological risk [27], and Chaharmahal and Bakhtiari province of Iran Cd have great ecological risk [28] The elements with ecological risk are different in different countries. Individual elements of soil heavy metals in Qianjin town have different levels of ecological risk in individual areas. The ecological risk level of Hg has reached a very strong level. It is suggested to take measures to prevent and control.

Health risk refers to the possibility of disease, disability and health loss caused by natural, social and human development factors in the process of human life. The maximum value of the total non-carcinogenic health risk index of heavy metal children in the study area is 5.47, indicating that there is a non-carcinogenic health risk; The average value of the total carcinogenic risk index for adults is 9.97E-06, and the maximum value is 1.50E-05. The average value of the total carcinogenic risk index for children is 2.68E-05, and the maximum value is 4.04E-05. The carcinogenic risk index for adults and children exceeds the soil treatment benchmark value $10^{-6}$ proposed by the United States EPA. Therefore, prevention should be strengthened. Considering the importance of the study area and the current situation of heavy metal pollution, it is suggested to introduce prevention and control mechanisms. Feng et al. (2021) [29], Deep et al. (2021) [30], Wu et al. (2017) [31] some scholars tried to introduce bioavailability and found that the non-carcinogenic risk and carcinogenic risk of heavy metals to adults and children would be greatly reduced. Dalia et al. (2021) [32] proposed two kinds of algae dry matter for bioremediation of heavy metal contaminated soil, and achieved good results. Fassler et al. (2010) [33] used sunflower, corn and tobacco to manage the plants in heavy metal polluted farmland. The research thinks that it will take several centuries for plant extraction to be used for soil purification.

Generally speaking, soil heavy metal pollution is widespread in all parts of the world. There is heavy metal pollution in the black soil area of Northeast China, and there are also ecological and health risks caused by heavy metal pollution. The prevention and control should not be slackened. Especially for the important grain producing area such as black soil region, it is necessary to improve ideological understanding, improve laws and regulations, formulate norms and standards, research and develop methods and technologies, and carry out scientific prevention and control of heavy metal pollution.

## Conclusion

China's cold black soil region, an important commodity grain base, has been polluted by heavy metals to varying degrees. The average value of the content of eight heavy metals is higher than its background value. Among them, the accumulation degree of Cr is the highest, the content is between 31.37 and 84.38 mg/kg, and the average value is 65.06 mg/kg, which is 1.53 times of its soil background value. Compared with 2010, the content of five heavy metal elements (As, Cu, Hg, Pb, Zn) increased, and the increase of Hg was the largest, 1.33 times that of 2010. Under the influence of human activities, the content of heavy metals in surface soil is increasing, and the heavy metals in farmland soil are obviously affected by human activities. From the perspective of potential ecological risk of single heavy metal, Hg hazard index is the highest, with an index range of 22.93~655.482, with slight, medium, strong, very strong and extremely strong ecological risks, covering all ecological risk levels, followed by Cd with strong ecological risks, mainly with slight and medium risks, Pb with slight and strong ecological risks, mainly with slight ecological risks, and Cr, as, Ni, Zn and Cu with slight ecological risks. In general, Hg and Cd are the main influencing elements of shallow soil ecological hazards. There is no non-carcinogenic risk of heavy metals to adult health, but there is non-carcinogenic risk to children. The carcinogenic risk index of adults and children exceeds the soil treatment benchmark value $10^{-6}$ proposed by EPA of the United States. As is the element that has the greatest impact on the non-carcinogenic health risk and carcinogenic health risk of adults and children.

## Acknowledgments

This paper is inspired by Mr. Hao Ziguo. I would like to thank the Northeast Geological Science and Technology Innovation Center Project of the China Geological Survey (QCJJ2022-43), the Natural Resources Comprehensive Survey Project (DD20211589), and the Hydrogeological Survey Project (DD20230470) for their support. Thank you for the help of editors and anonymous experts.

## Funding

This research was funded by the funding project of Northeast Geological S&T Innovation Center of China Geological Survey（QCJJ2022-43）, the Natural Resources Comprehensive Survey Project (DD20211589), and the Hydrogeological Survey Project (DD20230470).

## Availability of Data and Material

The data and material data provided by the laboratory of Harbin natural resources comprehensive survey center are reliable.

## Author Contributions

Sun Qifa (1966 -), male, doctor., Professor level senior engineer, mainly engaged in hydrogeology, engineering geology, environmental geology and geochemical investigation and research, mailing address: No. 1, Baojianfu Road, Nangang District, Heilongjiang Province, email: 152468435@qq.com

All authors Qifa Sun e-mail: 152468435@qq.com, Ke Yang e-mail: yangkejs@qq.com, Zhuoan Sun e-mail: 1144746765@qq.com, Jianheng Wang e-mail: sun99-99@163.com Weiguo Xing e-mail: 2408806234@qq.com, Guojie Hao e-mail:2208408367@qq.com

## Conflicts of Interest

There is no conflict of interest in the article.

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