# HUMAN HEALTH RISK ASSESSMENT FOR CHEMICAL POLLUTANTS IN DRINKING WATER SOURCE IN SHIZUISHAN CITY, NORTHWEST CHINA

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Received 22 May 2010; revised 19 November 2010; accepted 18 December 2010

## ABSTRACT
Human health is closely related with the quality of drinking water. Various chemical pollutants in the drinking water can cause great risk to human health. Shizuishan city is an important coal-based industrial city where residents mainly rely on groundwater. In order to protect the safety of water supply, based on the sample survey, health risk assessment model recommended by the Unites States Environmental Protection Agency was adopted to assess the health risks of groundwater in the region. During the study, total 25 groundwater samples were colleted from drinking water supply wells and many parameters such as $Cr^{6+}$, fluoride, arsenide, volatile phenol and cyanide were examined according to standard procedures recommended by Chinese Ministry of Water Resources. Evaluation results showed that the greatest risk value due to non-carcinogenic pollutants was caused by fluoride, while the greatest health risk due to chemical carcinogenic pollutants was primarily caused by $Cr^{6+}$, the second was arsenide. The health risk due to chemical carcinogens was 3 magnitudes larger than that caused by non-carcinogenic pollutants, which indicated that chemical carcinogens were the primary pollutants in the drinking groundwater. The total health risk level was within the acceptable level proposed by Unites States Environmental Protection Agency, but exceeded the acceptable level recommended by International Commission on Radiologic Protection which meant that the groundwater needs pretreatment before consumption.

**Key words**: Health risk assessment; Water quality; Pollutants; Drinking water source; Shizuishan City

## INTRODUCTION
Human health risk assessment is defined as the process to estimate the nature and probability of adverse health effects in humans who may be exposed to chemicals in contaminated environmental media, now or in the future, by the Unites States Environmental Protection Agency (USEPA). Health risk assessment sprang up during the 1980s (Huang *et al*., 2008). It involves identifying the potential of a risk source to introduce risk agents into the environment, estimating the amount of risk agents that come into contact with the human-environment boundaries and quantifying the health consequence of exposure (Ma *et al*., 2007).

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To fulfill the health risk assessment, generally four steps must be followed: hazard identification, dose-response assessment, exposure assessment and risk characterization (Momot and Synzynys, 2005). Since the birth of health risk assessment, it has drawn a lot of attention from many scientists across the world and many assessments relating to drinking purpose and human health have been reported. Kim *et al*. (2004) analyzed the radiologic and chemical risks of uranium in drinking groundwater in Korea and found that exposure to uranium was unlikely to pose an adverse health risk. Falconer and Humpage (2005) performed the health risk assessment of cyanobacterial toxins in drinking water in South Australia. Alam *et al*. (2006) carried out a study of the water quality conditions of Sylhet city of Bangladesh and its restaurants and assessed the risks to human health. At the same time in China, massive studies have been done on health risk assessment. Zhang *et al*. (2007) performed heath risk assessment of drinking water using the Multimedia Contaminant Fate, Transport, and Exposure Model (MMSOILS). Li and Tian (2008) analyzed health risk caused by heavy metals in a water source and found the health risk comparisons caused by gene toxic substances was $Cr^{6+}$>As>Cd and risk comparisons caused by body toxic substances was Pb>Cu>Hg. Li *et al*. (2010) performed groundwater quality assessment for drinking purpose with improved WQI method in an area of Northwest China. Ni *et al*. (2010) studied the health risk in two lake sources and found that arsenide and $Cr^{6+}$ were the major pollutants that threatened human health.

Shizuishan city is an important industrial city mostly depending on coal industry and chemical engineering. It is located in arid Northwest China where groundwater plays a key role in the development of economy and society. The groundwater quality is closely related to human health. However, with the influence of human activities, the water quality is becoming worse and worse. Although some work has been done in this region on the groundwater quality assessment, no work on human health risk has been implemented till now. In this paper, the health risk assessment model proposed by USEPA was used to assess the health risk in Shizuishan city for the purpose of providing theoretical basis for drinking groundwater protection and monitoring.

## MATERIALS AND METHODS

*Overview of the study area*

Shizuishan city is located in the northern part of Ningxia Hui Autonomous Region. It is an important industrial city in Ningxia. Coal industry and chemical engineering industry are the major industries supporting the local economy. Dawukou District is the political, economic and cultural center of Shizuishan city. It covers a total area of 1008 $km^2$ with a total population of 0.259 million. The study area is shown in Fig. 1. Located in arid and semi-arid areas, the climate here is a typical continental climate with abundant sunshine, concentrated rainfall, strong evaporation and dry air. The average annual temperature varies between (8.4~9.9)ºC, the average annual minimum temperature varies between (-19.4-23.2)ºC and the highest average annual temperature changes between (32.4-36.1)ºC. Annual precipitation is 160.94 mm and precipitation usually concentrates in July to September. The average annual evaporation is 1792.64mm which is 11 times of the rainfall. The average relative humidity is 47%. Benefiting from the Yellow River, many drains go across the study area. Alluvial-pluvial oblique plain and alluvial-lacustrine plain, flat and open, are the dominated landforms formed by thick unconsolidated sediments during Quaternary period.

There are two major sources for water supply in the region. One is pumping river water from the Yellow River, the other is from groundwater. As the water pumped from the Yellow River is not fit for direct drinking, it is mainly used for agricultural usage and industrial usage, and groundwater is used for domestic usage and industrial usage. It is reported that over 89% of drinking water in the region is from groundwater. Hence, groundwater quality is vital to people's health.

*Materials*

For this study, a total of 25 water samples were collected from 25 different water supply wells during August 2009 to December 2009. These wells were named with different types of numbers because they were constructed in different years and by different constructors. Of the 25 samples, sample W52, W58, W60, W62, W66, YW06, 13 -A, 9-A, 7-A, 8-A, 12-A and Well 2 were collected in the shallow aquifer (80-150 m) and sample W51, W57, W59, W61, W65, W67, YW07, 6-B, 8-B, 9-B, Z-1, Well 1 and Well 2 were collected in deep aquifer (170-240 m).

Samples were collected in pre-cleaned plastic polyethylene bottles for physicochemical analysis of sample. Prior to sampling, all the sampling containers were washed and rinsed thoroughly with the groundwater to be taken for analysis. All the water samples were analyzed by Laboratory of Urban Water Quality Monitoring Network in Ningxia Shizuishan Stations for various chemical parameters in accordance with standard procedures recommended by Chinese Ministry of Water Resources (results are listed in

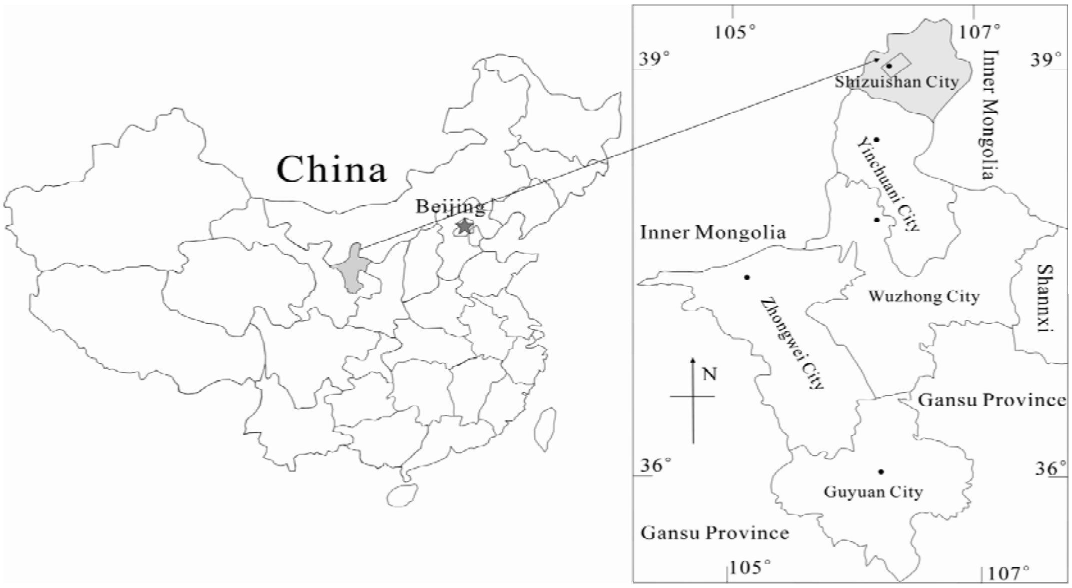


Fig. 1: Location of study area

Table 1). During sample collection, handling, and preservation, standard procedures recommended by the Chinese Ministry of Water Resources were followed to ensure data quality and consistency. According to Chinese Standards for Drinking Water Quality, all the parameters are within the limits of the standards. However, this does not necessarily mean that no health risk exist, because a small dose of intake of these pollutants will also cause health problems due to long-term intake.

*Methods*

Generally, the toxic substances can be classified into two kinds: carcinogenic and non-carcinogenic substances. Carcinogenic substances can be further subdivided into chemical carcinogenic substances and radioactive pollutants. Usually radioactive pollutants are rare and can not be detected, so the assessment generally can be classified accordingly into chemical carcinogenic risk assessment and the non-carcinogenic risk (Huang *et al*., 2006; Ni *et al*., 2009).

The chemical carcinogenic risk assessment can be described as follows (Ni *et al*., 2009):

$$R^c = \sum_{i=1}^{k} R_i^c \quad (1)$$

$$R_i^c = [1-\exp(-D_i q_i)]/A \quad (2)$$

$$D_i = Q \times C_i / W \quad (3)$$

Where, $R_i^c$ is the carcinogenic pollutant *i* to the average individual carcinogenesis annual risk by pathway-intake; $D_i$ is the carcinogenic pollutant *i* to the daily average exposure dosage per unit weight by the pathway-intake; $q_i$ is the carcinogenic coefficient of carcinogenic pollutant *i* by the pathway-intake; *A* in equation (2) is the average span of human while *W* in equation (3) is average weight of human; *Q* is the average daily intake of drinking water for an adult; $C_i$ is the concentration of carcinogenic pollutant *i*.

The non-carcinogenic risk assessment is usually expressed as below (Ni *et al*., 2009):

$$R^n = \sum_{j=1}^{n} R_j^n \quad (4)$$

$$R_j^n = (Dj/D_{jRf}) \times (10)^{-6} / A \quad (5)$$

$$D_j = Q \times C_j / W \quad (6)$$

Where, $R_j^n$ is the non-carcinogenic pollutant *j* to the average individual carcinogenic risk by pathway-intake annually; $D_j$ is the non-carcinogenic pollutant *j* to the daily average exposure dosage per unit weight by the pathway-intake; $D_{jRf}$ is the to reference dosage of non-carcinogenic pollutant *j*; *A* in equation (5) is the average span of human; *W* in equation (6) is average weight of human; *Q* is the average daily intake of drinking water for an adult; $C_j$ is the concentration of non-carcinogenic pollutant *j*.

Table 1: Monitoring data of water quality in drinking water source and limits of standards (mg/L)

| Sample ID | F | Volatile phenol | Cyanide | As | $Cr^{6+}$ | Hg | Pb | Cd |
|---|---|---|---|---|---|---|---|---|
| Standards | ≤1.0 | ≤0.002 | ≤0.05 | ≤0.01 | ≤0.05 | ≤0.001 | ≤0.01 | ≤0.005 |
| W51 | 1.12 | 0.002 | 0.002 | 0.00061 | 0.004 | 0.000024 | 0.00070 | 0.000284 |
| W52 | 0.98 | 0.002 | 0.002 | 0.00120 | 0.004 | 0.000153 | 0.00089 | 0.000479 |
| W57 | 1.22 | 0.002 | 0.002 | 0.00251 | 0.004 | 0.000036 | 0.00070 | 0.000480 |
| W58 | 1.41 | 0.002 | 0.002 | 0.00114 | 0.002 | 0.000051 | 0.00070 | 0.000200 |
| W59 | 1.41 | 0.002 | 0.002 | 0.00190 | 0.001 | 0.000013 | 0.00070 | 0.000339 |
| W60 | 1.20 | 0.002 | 0.002 | 0.00136 | 0.002 | 0.000045 | 0.00070 | 0.000311 |
| W61 | 1.12 | 0.002 | 0.002 | 0.00088 | 0.002 | 0.000073 | 0.00070 | 0.000233 |
| W62 | 1.00 | 0.002 | 0.002 | 0.00111 | 0.004 | 0.000047 | 0.00070 | 0.000356 |
| W65 | 1.38 | 0.002 | 0.002 | 0.00031 | 0.004 | 0.000255 | 0.00070 | 0.000266 |
| W66 | 1.04 | 0.002 | 0.002 | 0.00132 | 0.004 | 0.000108 | 0.00070 | 0.000198 |
| W67 | 1.17 | 0.002 | 0.002 | 0.00031 | 0.004 | 0.000578 | 0.00070 | 0.000130 |
| YW06 | 0.71 | 0.004 | 0.003 | 0.00080 | 0.000 | 0.000100 | 0.01000 | 0.000500 |
| YW07 | 0.57 | 0.001 | 0.003 | 0.00300 | 0.000 | 0.000010 | 0.01000 | 0.000500 |
| 13-A | 0.6 | 0.002 | 0.002 | 0.00031 | 0.004 | 0.000054 | 0.00070 | 0.000341 |
| 9-A | 1.35 | 0.002 | 0.002 | 0.00178 | 0.004 | 0.000013 | 0.00070 | 0.000210 |
| 9-B | 1.51 | 0.002 | 0.002 | 0.00289 | 0.004 | 0.000013 | 0.00162 | 0.000307 |
| 6-B | 0.72 | 0.002 | 0.002 | 0.00254 | 0.004 | 0.000013 | 0.00070 | 0.000381 |
| 8-A | 0.68 | 0.002 | 0.002 | 0.00254 | 0.004 | 0.000076 | 0.00147 | 0.000266 |
| 7-A | 0.87 | 0.002 | 0.002 | 0.00258 | 0.004 | 0.000013 | 0.00070 | 0.000223 |
| 8-B | 0.62 | 0.002 | 0.002 | 0.00196 | 0.004 | 0.000013 | 0.00070 | 0.000301 |
| Z-1 | 0.58 | 0.002 | 0.002 | 0.00031 | 0.004 | 0.000037 | 0.00070 | 0.000333 |
| 12-A | 1.41 | 0.002 | 0.002 | 0.00525 | 0.018 | 0.000450 | 0.00070 | 0.000383 |
| Well 1 | 1.05 | 0.002 | 0.002 | 0.00214 | 0.004 | 0.000400 | 0.00070 | 0.000132 |
| Well 2 | 0.45 | 0.002 | 0.002 | 0.00209 | 0.004 | 0.000013 | 0.00241 | 0.000130 |
| Well 3 | 0.52 | 0.002 | 0.002 | 0.00697 | 0.004 | 0.000407 | 0.00070 | 0.000130 |

The carcinogenic coefficients and the reference dosage are important parameters regarding to the health risk assessment. During the calculation processes, $q_i$ and $D_{jRf}$ are adopted from USEPA Guidelines for Carcinogen Risk Assessment and are listed in Tables 2 and 3. According to statistical investigation, the values of $Q$, $W$ and $A$ are assigned as 2, 70, 70, respectively.

The cumulative effects of the toxic substances usually include addition relation, cooperating relation and resisting relation. Cumulative effects analysis is a very complicated and uncertain work.

So far, no systematic theory and method has been found about the cumulative effects. In this paper, it was assumed that each contamination is independent and the relation of cumulative effects among these toxic substances is addition relation. Hence, the total risk can be obtained by adding chemical carcinogenic risk with non-carcinogenic risk, that is:

$$R = R^c + R^n = \sum_{i=1}^{k} R_i^c + \sum_{j=1}^{n} R_j^n \tag{7}$$

Table 2: Reference dosage of non-carcinogens $D_{jRf}$ mg/kg·d

| non-carcinogens | Volatile | Cyanide | Hg | Pb | F |
|---|---|---|---|---|---|
| $D_{jRf}$ | $1.0\times10^{-1}$ | $3.7\times10^{-2}$ | $3.0\times10^{-4}$ | $1.4\times10^{-3}$ | $6.0\times10^{-2}$ |

Table 3: Carcinogenic coefficients of chemical carcinogens $q_i$ mg/kg·d

| Chemical carcinogens | As | $Cr^{6+}$ | Cd |
|---|---|---|---|
| $q_i$ | 15 | 41 | 6.1 |

## RESULTS

Based on the above-mentioned methods and recommended parameters, non-carcinogenic risk and chemical carcinogenic risk as well as the total health risk were respectively calculated and the results were shown in Table 4.

It can be seen from Table 4 that in the investigation area, the greatest risk value due to non-carcinogenic pollutants is caused by fluoride, ranging within $1.84\times10^{-8}$~$6.16\times10^{-8}$ per year. Among the three kinds of chemical carcinogenic pollutants, the

Table 4: Calculation results of health risk

| ID | F $10^{-8}$/a | Volatile phenol $10^{-11}$/a | Cyanide $10^{-10}$/a | Hg $10^{-10}$/a | Pb $10^{-9}$/a | Cd $10^{-7}$/a | As $10^{-5}$/a | $Cr^{6+}$ $10^{-5}$/a | $R^n$ $10^{-8}$/a | $R^c$ $10^{-5}$/a | $R$ $10^{-5}$/a |
|---|---|---|---|---|---|---|---|---|---|---|---|
| W51 | 4.57 | 4.90 | 1.32 | 1.47 | 1.22 | 7.07 | 0.37 | 6.68 | 4.73 | 7.12 | 7.13 |
| W52 | 4.00 | 4.90 | 1.32 | 9.37 | 1.55 | 11.93 | 0.73 | 6.68 | 4.27 | 7.53 | 7.54 |
| W57 | 4.98 | 4.90 | 1.32 | 2.20 | 1.22 | 11.95 | 1.54 | 6.68 | 5.14 | 8.33 | 8.34 |
| W58 | 5.76 | 4.90 | 1.32 | 3.12 | 1.22 | 4.98 | 0.70 | 3.34 | 5.93 | 4.09 | 4.10 |
| W59 | 5.76 | 4.90 | 1.32 | 0.80 | 1.22 | 8.44 | 1.16 | 1.67 | 5.90 | 2.92 | 2.93 |
| W60 | 4.90 | 4.90 | 1.32 | 2.76 | 1.22 | 7.74 | 0.83 | 3.34 | 5.07 | 4.25 | 4.26 |
| W61 | 4.57 | 4.90 | 1.32 | 4.47 | 1.22 | 5.80 | 0.54 | 3.34 | 4.76 | 3.94 | 3.94 |
| W62 | 4.08 | 4.90 | 1.32 | 2.88 | 1.22 | 8.86 | 0.68 | 6.68 | 4.25 | 7.45 | 7.45 |
| W65 | 5.63 | 4.90 | 1.32 | 15.61 | 1.22 | 6.62 | 0.19 | 6.68 | 5.93 | 6.93 | 6.94 |
| W66 | 4.24 | 4.90 | 1.32 | 6.61 | 1.22 | 4.93 | 0.81 | 6.68 | 4.45 | 7.54 | 7.54 |
| W67 | 4.78 | 4.90 | 1.32 | 35.39 | 1.22 | 3.24 | 0.19 | 6.68 | 5.27 | 6.90 | 6.91 |
| YW06 | 2.90 | 9.80 | 1.99 | 6.12 | 17.49 | 12.45 | 0.49 | 0.00 | 4.74 | 0.61 | 0.62 |
| YW07 | 2.33 | 2.45 | 1.99 | 0.61 | 17.49 | 12.45 | 1.84 | 0.00 | 4.10 | 1.96 | 1.96 |
| 13-A | 2.45 | 4.90 | 1.32 | 3.31 | 1.22 | 8.49 | 0.19 | 6.68 | 2.62 | 6.95 | 6.96 |
| 9-A | 5.51 | 4.90 | 1.32 | 0.80 | 1.22 | 5.23 | 1.09 | 6.68 | 5.66 | 7.82 | 7.83 |
| 9-B | 6.16 | 4.90 | 1.32 | 0.80 | 2.83 | 7.64 | 1.77 | 6.68 | 6.47 | 8.52 | 8.53 |
| 6-B | 2.94 | 4.90 | 1.32 | 0.80 | 1.22 | 9.49 | 1.55 | 6.68 | 3.09 | 8.33 | 8.33 |
| 8-A | 2.78 | 4.90 | 1.32 | 4.65 | 2.57 | 6.62 | 1.55 | 6.68 | 3.10 | 8.30 | 8.30 |
| 7-A | 3.55 | 4.90 | 1.32 | 0.80 | 1.22 | 5.55 | 1.58 | 6.68 | 3.70 | 8.31 | 8.32 |
| 8-B | 2.53 | 4.90 | 1.32 | 0.80 | 1.22 | 7.49 | 1.20 | 6.68 | 2.68 | 7.95 | 7.96 |
| Z-1 | 2.37 | 4.90 | 1.32 | 2.27 | 1.22 | 8.29 | 0.19 | 6.68 | 2.53 | 6.95 | 6.95 |
| 12-A | 5.76 | 4.90 | 1.32 | 27.55 | 1.22 | 9.54 | 3.21 | 29.81 | 6.17 | 33.11 | 33.12 |
| Well 1 | 4.29 | 4.90 | 1.32 | 24.49 | 1.22 | 3.29 | 1.31 | 6.68 | 4.67 | 8.02 | 8.03 |
| Well 2 | 1.84 | 4.90 | 1.32 | 0.80 | 4.22 | 3.24 | 1.28 | 6.68 | 2.28 | 7.99 | 7.99 |
| Well 3 | 2.12 | 4.90 | 1.32 | 24.92 | 1.22 | 3.24 | 4.26 | 6.68 | 2.51 | 10.97 | 10.97 |
| Mean | 4.03 | 5.00 | 1.38 | 7.33 | 2.78 | 7.38 | 1.17 | 6.47 | 4.40 | 7.71 | 7.72 |

risk value caused by $Cr^{6+}$ is the greatest, ranging within 0~29.81×10$^{-5}$ per year. The ranking of health risk according to the mean value is as follows: $Cr^{6+}$>As>Cd>F>Hg>cyanide>volatile phenol. From Table 4, it can also be seen that the values of chemical carcinogenic risk are much larger than values of non-carcinogenic risk. This indicates apparently that chemical carcinogenic pollutants in the drinking groundwater are the major health risk inducing chemical parameters.

The human health risks in different wells are different from each other, and in some wells, the human health risks may be higher than that in other wells. This can be attributed to the chemical carcinogenic pollutants in the well. For example, sample 12-A possesses the highest health risk in the area, and the highest human health risk is 33.12×10$^{-5}$ per year. It can be seen form Table 4 that the chemical carcinogenic risk, a major part of the total health risk, is also the highest in sample 12-A. The lowest total human health risk is 0.62×10$^{-5}$ per year appearing in sample YW06, and the chemical carcinogenic risk in YW06 is 0.61×10$^{-5}$ per year which is the lowest among all the samples.

## DISCUSSION

Non-carcinogenic risk and chemical carcinogenic risk as well as the total health risk were respectively calculated. The level of human health risk caused by non-carcinogenic pollutants ranges within 2.28×10$^{-8}$~6.47×10$^{-8}$ per year. That is to say, the deaths because of non-carcinogenic pollutants in each 100 million are about 2 to 6 persons, the risk is acceptable and even can be ignored. On the other side, the risk level because of chemical carcinogens is 0.61×10$^{-5}$~33.11×10$^{-5}$ per year which is over 5×10$^{3}$ times of that caused by non-carcinogenic pollutants. This data means that 6~331 persons in each million will die because of drinking the water and the conclusion is fearful and can not be acceptable. The water really needs some degree of pretreatment before consumption. The results also reveal that the health risk is caused mainly by chemical carcinogenic pollutants.

According to United States Environmental Protection Agency (USEPA), the acceptable health risk level is 10$^{-6}$~10$^{-4}$ per year. The total risk of pumping wells and mean total risk are shown in Fig. 2 From Fig. 2, it may be observed that in most water supply wells, the health risk is within the recommended level of USEPA but

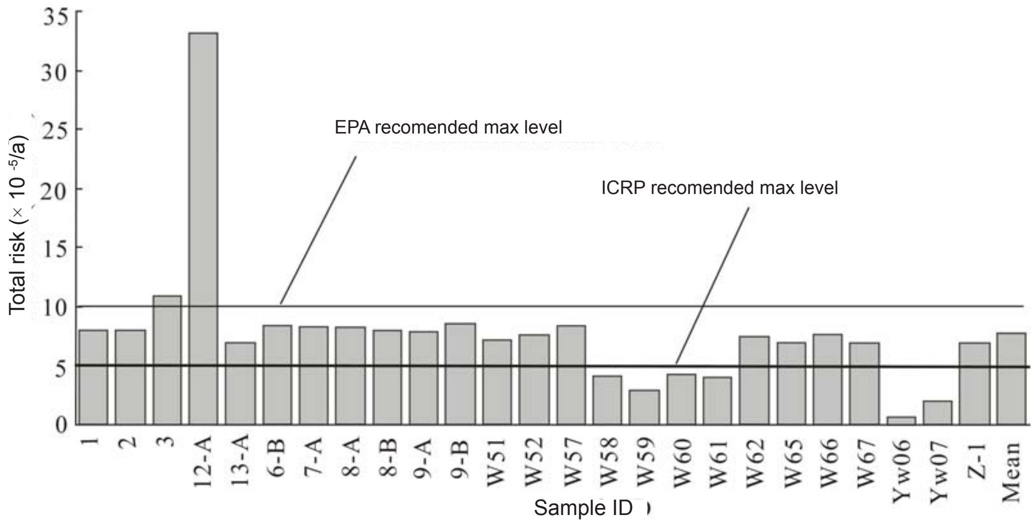


Fig 2: Total risk of pumping wells and mean total risk

surpasses the maximum level ($5\times10^{-5}$ per year) recommended by International Commission on Radiologic Protection (ICRP). The annually mean total health risk in the region is $7.72\times10^{-5}$ which is within the acceptable level of USEPA. However, it surpasses the ICRP recommended level which means the groundwater need pretreatment before consumption.

Compared with a similar research conducted by Wei *et al*. (2008) in Yinchuan City, an adjacent city in Northwest China, the assessed human health risk in this paper is a little higher than that in their study. In their study, the highest total human health risk was $8.47\times10^{-5}$ per year and the average human health risk was $5.47\times10^{-5}$ per year, while in this study, the highest total human health risk was $33.12\times10^{-5}$ per year and the average human health risk was $7.72\times10^{-5}$ per year. This may be attributed to the intensive mining and severe polluting chemical engineering factories in the area. In spite of this, there still are some similar results. Both studies prove that human health risk caused by non-carcinogenic pollutants is acceptable and even can be ignored, and the human health risk is mainly caused by chemical carcinogenic pollutants. The ranking of health risk caused by $Cr^{6+}$, As and Cd is as follows: $Cr^{6+}$>As>Cd. Moreover, the several studies carried out in China that have been introduced in INTRODUCTION also showed that $Cr^{6+}$ is the major pollutant with regard to human health risk in major water source in China. This reminds us more attention should be focused on $Cr^{6+}$ pollution in the groundwater as well as some other chemical carcinogenic pollutants.

Take the whole analysis into consideration, it is recommended that chemical carcinogens are the primary pollutants that cause the health risk in the region and should be treated before consumption to decrease the risk. At the same time, measures of groundwater quality protection and monitoring should be enhanced and new water supply source which has lower health risk must be in consideration as well.

## ACKNOWLEDGEMENTS

This research project was jointly funded by the National Natural Science Foundation of China (Grant No. 40772160), Program for Changjiang Scholars and Innovative Research Team in University of Ministry of Education of China (Grant No. IRT0811), and Program of Introducing Talents of Discipline to Universities (111 Project) (Grant No. B08039). Authors also want to express their sincere appreciation to the anonymous reviewers for their useful comments on the manuscript.

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