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Health Risk Assessment of Nitrate Contamination in Groundwater: A Case Study of an Agricultural Area in Northeast China

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Abstract High levels of nitrates in groundwater pose a risk to human health. In this study, we selected areas with typical agricultural nitrate pollution in northeast China as study sites. We then collected groundwater samples for nitrate nitrogen content analysis using the Four Step method developed by the United State Environmental Protection Agency (USEPA) in conjunction with the non-carcinogens health risk model (R=CDI/RfD) to determine the health risk associated with nitrate pollution of groundwater. The reference value of nitrates in drinking water was set at 10 mg/L (measured as nitrogen) and the intake reference dose of nitrate was set at 1.6 $mg{\bullet}kg^{-1}{\bullet}d^{-1}$ based on the EPA's IRIS(Integrated Risk Information System). The water intake reference values were set at 2.3 L/d and 1.5 L/d based on the EPA values and actual values observed in the study area. The average exposure time was the ED (exposure duration)×365d/a. Weights refer to the 2002 national urban and rural average weight of residents of different genders and different ages. Health hazard index calculation was based on the above information, and the index less than 1 is acceptable (U.S. EPA's Risk Assessment Guide). Health risk assessment maps were then drawn by Arcgis software. The results indicated that agricultural sewage irrigation areas in the study area showed strong health risks, but that those of the city were relatively small. Moreover, the results indicated that children's health risks are greater than those of adults.

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1 Introduction

Continued nitrogen emissions by various sources of pollution pose a risk to groundwater and have become a widespread problem worldwide (Samuel Mattern et al. 2009; Rodvang and Simpkins 2001; Burow et al. 2010; Panagopoulos et al. 2011). Over the past few decades, excessive use of nitrogen has caused agricultural non-point source pollution to become one of the most important modes of contamination of regional groundwater. According to 2004 statistics, China is the world's largest fertilizer producer and consumer. In 2002, a total of 142 million tons of fertilizer were consumed worldwide, with 43.395 million tons being consumed in China (Zhu Zhaoliang and David North 2004). This large-scale use of chemical fertilizers has led to increasing groundwater nitrate pollution. According to the findings of the Chinese Academy of Agricultural Sciences in the five provinces of the northern 20 counties in more than 800 survey sites, the groundwater nitrate content of 45 % of the survey points (N) was greater than 11.3 mg/L, while it was more than 20 mg/L at 20 % of the sites and higher than 70 mg/L at some individual survey points (Zhaoliang and North 2004). It has been reported that a drinking water nitrate nitrogen content of more than 10 mg/L can cause methemoglobinemia (Federal-Provincial Working Group on Drinking Water (Canada) (Health and Welfare Canada 1979). A geological survey of Shenyang in 2009 and 2010 indicated that the groundwater in the study area currently has a groundwater nitrate content (N) range of 0–157.02 mg/L, and that areas characterized by excessive groundwater nitrate include sewage irrigation areas, which are common sources of agricultural pollution. Groundwater nitrate pollution is threatening human health and safety; therefore, it is necessary to expand the health risk assessment of groundwater nitrate pollution and provide a reference for groundwater management and pollution prevention.

In the past few decades there has been a growing awareness of the health hazards of chemicals present in the environment (Davis et al. 2001). Accordingly, researchers have reviewed early risk assessment techniques. Since the United States Environmental Protection Agency (USEPA) promulgated the Interim Procedures and Guidelines for Health Risk and Economic Impact Assessments of Suspected Carcinogens (Train 1976) in 1976, strict health and economic impact risk assessments have been an important part of the regulatory process. Subsequently, the EPA generated water quality standards for 64 contaminants (USEPA 1980), as well as its first quantitative description of risk assessment. The groundwater nitrate health risk assessment model used in the present study is based on integrating the principles of risk assessment from a report published by the National Academy of Science (NAS): Risk Assessment in the Federal Government: Managing the Process (NRC 1983; commonly referred to as the Red Book) (USEPA 2001). According to this publication, human health risk assessment includes four steps:

1. Hazard Identification: The purpose of this step is to determine some of the adverse factors caused by exposure to some receptors, and provide strong evidence to demonstrate exposure.
2. Dose–response Assessment: The purpose of this step is to document the relationship between dose and toxic effect.
3. Exposure Assessment: The purpose of this step is to calculate a digital assessment of exposure or dose.
4. Risk Characterization: The purpose of this step is to summarize and integrate information from the preceding steps to synthesize an overall conclusion about risk.

2 Materials and Methods

2.1 Study Area

The study area is located south of northeast China. The study area is characterized by an overall topography that decreases gradually from northeast to southwest and an average ground elevation of 35–50 m. The study area is subject to a temperate monsoon climate, and has an average annual temperature of 6.2–9.7 °C. The eastern portion of the area has a hilly topography, while other areas are covered by Quaternary loose deposits. Quaternary deposits gradually thicken from east to west, and the sediment particles gradually transition to coarse sand from gravel, and then to medium and finally fine sand. Regional surface water bodies include the Hun River, which runs through the study area from northeast to southwest, with areas northwest and southeast of the study area containing a sewage river and sewage irrigation channels. Land use and the sampling point distribution are shown in Fig. 1, while Table 1 shows the fertilizer usage for the study area in 2011.

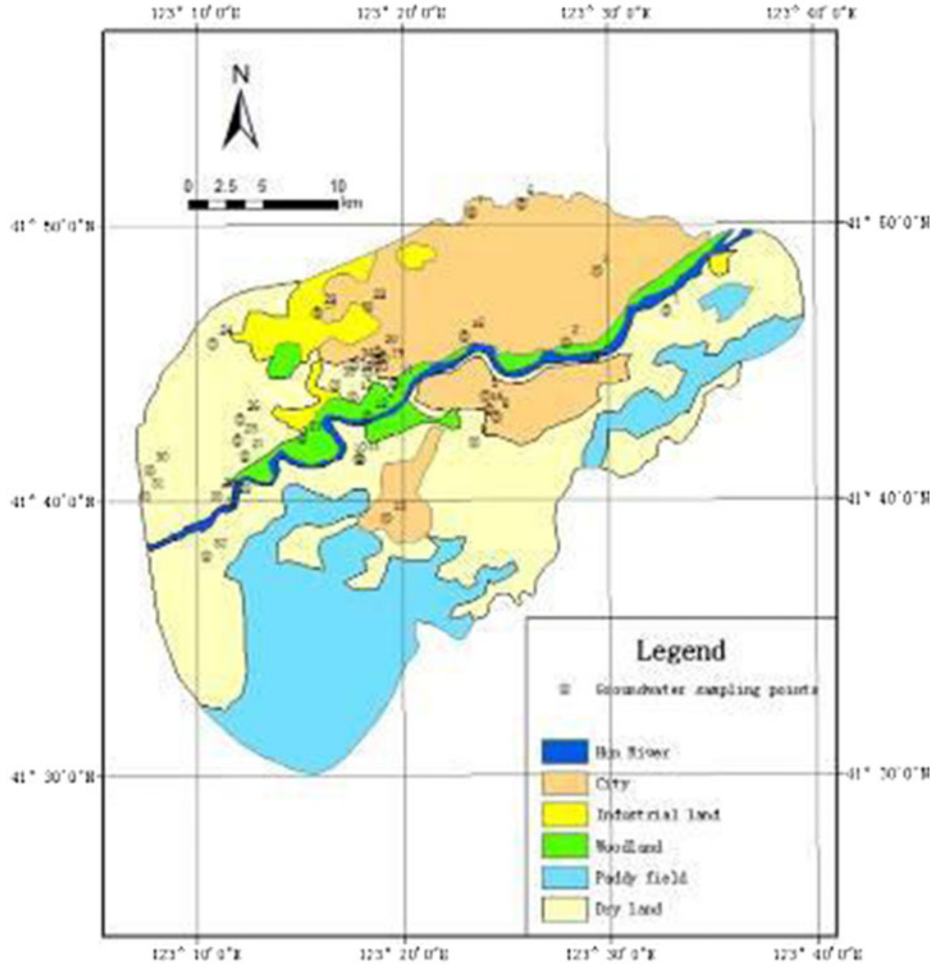

Fig. 1 Land use and sampling point distribution

Table 1 2011 Fertilizer use (tons)

Nitrogen aggregate	Farming	Forestry	Animal husbandry	Fisheries	Net amount
562363	553866	6907	403	1187	173208

2.2 Experimental

2.2.1 Sample Collection

Groundwater nitrate samples were collected in strict accordance with the technical standards of the China Geological Survey Evaluation Norms for groundwater pollution, and washed well before sample collection.

2.2.2 Test Method

Nitrate in water was measured based on ion chromatography using a Metrohm 861 consecutive dual-suppressed ion chromatograph, which had a detection limit of 0.01 to 0.02 mg/L. Analysis was conducted using an SA-8 anion column and conductivity detector, with 0.24 mol/L Na_2CO_3 solution and 0.30 mol/L $NaHCO_3$ solution at a ratio of 5.0 mL:10.0 mL as the eluent. The eluent was degassed and applied at a flow rate of 1.5 mL/min. The sample injection volume was 1 mL and samples were measured after direct injection.

2.2.3 Non-carcinogens Health Risk Model

Non-carcinogens health risk model (US.EPA) for nitrate health risk assessment:

$$R = CDI/RfD$$

Where: R-Non-Carcinogens Risk Quotient; CDI-Chronic Daily Intake (mg/kg•day); RfD -Reference Dose (mg/kg•day);

$$CDI = C_w \times WI \times F \times D/(W \times T)$$

Where: C_W-Chemicals Content in Water (mg/L); WI-Water Intake (L/d); F-Exposure Frequency (d/a); D- Exposure Duration (a/Lifetime); W-Weight (kg); T- Averaging Time (a)

3 Results and Analysis

3.1 Nitrate Content in Groundwater

As shown in Table 2, the total detectable rate of the nitrate in groundwater was 91.4 %, with 34.3 % of the samples exceeding the standard. These findings indicate that nitrate pollution in groundwater of the study area should not be ignored.

Table 2 Nitrate in groundwater

Item	Minimum concentration (mg/L)	Top concentration (mg/L)	Average (mg/L)	Detectable rate	Exceeding standard rate
Nitrate	<0.01	42.15	11.47	91.4 %	34.3 %

3.2 Health Risk Assessment

3.2.1 Health Risk of Nitrate in Groundwater

The risk of nitrate in groundwater occurs via two pathways. In the first, nitrate and nitrite salts are converted to nitrite (NO_2^-) which has the potential to change hemoglobin in red blood cells into methemoglobin. Accordingly, drinking contaminated water, eating spoiled vegetables, juice or preserved foods, and direct oral intake of sodium nitrite can cause methemoglobinemia. Furthermore, infants have lower B5 reductase activity in their red blood cells than adults; therefore, the risk posed to infants is much greater. Second, nitrite formed via reduction of nitrate in the human body can react with secondary amines to form nitrosamines, which can be carcinogenic.

As previously mentioned, the nitrite formed by nitrate reduction in the human body will react with the secondary amines to form nitrosamines, which can be carcinogenic. However, there is no conclusive evidence that nitrate and nitrite will cause cancer; thus, they are classified as carcinogenicity group D by the USEPA.

3.2.2 Dose–response Assessment of Nitrate

Comly (1945) found that infants were vomiting as a result of consumption of nitrates in well water, and reported that nitrate content in drinking water should not exceed 10 mg/L (measured as nitrogen).

In 1958, WHO (World Health Organization) published the International Standards for Drinking Water, which specified that, for infants less than 1 year old, water containing more than 50 mg/L–l00 mg/L nitrate had the potential to cause methemoglobinemia. In 1984, the Guidelines for Drinking-Water Quality (published by WHO) recommended value of nitrate in water was reduced to 10 mg/L (measured as nitrogen). The China Drinking Water Standards (GB5749-2006) set the nitrate limit in drinking water at 10 mg/L (measured as nitrogen), while the groundwater limit was 20 mg/L (measured as nitrogen).

According to the hazards of nitrate and reference value at home and abroad, we selected 10 mg/L as the standard for nitrate in water. The intake reference dose of nitrate was 1.6 $mg \cdot kg^{-1} \cdot d^{-1}$ (USEPA 2001).

3.2.3 Exposure Assessment

Exposure assessment aims to determine the pollutant exposure types and exposure dose. For different exposure assessments, the emphasis is on considering the effects of pollutants in different exposure pathways after different durations, and based on the frequency and exposure dose that the receptor is subjected to. Men are generally only exposed to nitrate via drinking water; therefore, the exposure pathway is ingestion of contaminated water.

Because nitrate is classified as a group D carcinogen, we selected the non-cancer hazard quotient for its carcinogenicity (USEPA).

a. Concentrations of Nitrate in Water (C_w)

The average content during the exposure period is usually used for determination of the chemical content of water bodies in health risk assessments; therefore, in this study we selected data generated in November and December.

b. Amount of drinking water

Water intake is directly related to the degree of receptor exposure to pollutants. There is insufficient data pertaining to the study area available for statistical analysis; therefore, the USEPA target reference values are given as the recommended values for drinking water: Daily 2 L for adults, infants and young children (body weight <10 kg) daily 1 L. Zhang (2007) give the recommended values (Table 3) (Zhang 2008, 2007).

Based on the data presented above, we selected 2.3 L/d for adults and 1.5 L/d for children.

c. Exposure frequency (F) and exposure duration (D)

Exposure frequency is the frequency of receptor exposure to toxic pollutants. Because nitrates enter the body through drinking water, in this study we selected 365d/a. Exposure duration is the time for which the receptors are exposed. Taking into account population migration, the EPA gives the reference values listed in Table 4 (HHRAP Chapter 6: Quantifying Exposure 04-04-2012).

d. Weight

The weight data were based on the 2002 national urban and rural average weights of residents of different genders and ages (Zhang 2008).

The regional population distribution and proportion of sex and age for the study area (Shenyang) are presented in Tables 5 and 6.

Based on the above information, we selected an urban average adult weight of 54 kg and a rural average adult weight of 59 kg. Because limited data were available for children, we selected a conservative value of 35 kg.

e. Averaging time

For non-carcinogenic substances, the EPA generally uses the value of ED (exposure duration)×365d/a as the average exposure time (the EPA 1989e; 1991d).

Table 3 Recommended Drinking Water Values for Different Age Groups (Zhang. 2007)

Age Group	Average Value	Percentage Distribution		
		50th	90th	95th
<1 year old	0.3 L/d	0.24 L/d	0.65 L/d	0.76 L/d
<3 year old	0.61 L/d	–	1.5 L/d	–
3~5 year old	0.87 L/d	–	1.5 L/d	–
5~10 year old	0.74 L/d	0.66 L/d	1.3 L/d	1.5 L/d
11~19 year old	0.97 L/d	0.87 L/d	1.7 L/d	2.0 L/d
Youth	1.4 L/d	1.3 L/d	2.3 L/d	–
pregnant woman	1.2 L/d	1.1 L/d	2.2 L/d	2.4 L/d
Breast Feeding Women	1.3 L/d	1.3 L/d	1.9 L/d	2.2 L/d
Young people (heat or strenuous activity)	0.21~0.65 L/h			
Young people (activity)	6 L/d(Normal weather)~11 L/d (Very Hot Weather)			

Table 4 Reference values for exposure duration

Exposure Receptor	Exposure Duration (a)	Sources of reference values
Child Resident	6	U.S.EPA 1990f;1994r
Adult Resident	30	U.S.EPA 1990f;1994r
Fisher	30	U.S.EPA 1990f;1994r
Fisher Child	6	the same as Child Resident
Farmer	40	U.S.EPA 1990l;1994r
Farmer child	6	the same as Child Resident

3.2.4 Risk Characterization

Based on all of the aforementioned information, we obtained a health hazard index, R, which represents the non-carcinogenic health risk level. An R<1 indicates relatively safe conditions (EPA 1991d). Figure 2 shows the distribution of adult health risk assessment, while Fig. 3 shows that of children.

Table 5 2002 National urban and rural average weight of residents of different genders and ages

2002 national urban and rural average weight of residents of different genders, different ages

Age	Weight(kg)				Age	Weight(kg)			
	Rural Male	Rural Female	Urban Male	Urban Female		Rural Male	Rural Female	Urban Male	Urban Female
1 month old	5.3	5.3	5.4	5.2	9 year old	30.4	28.6	26.1	25.4
2 month old	6.3	6.0	6.2	5.6	10 year old	33.8	32.8	28.6	28.2
3 month old	7.1	6.8	6.9	6.3	11 year old	37.4	36.7	31.9	31.8
4 month old	7.6	6.8	7.5	7.3	12 year old	40.5	40.5	35.4	35.8
5 month old	8.3	7.6	8.0	7.4	13 year old	44.9	44.5	39.3	40.5
6 month old	8.7	8.3	8.6	8.1	14 year old	49.4	47.2	45.1	44.1
8 month old	9.5	9.0	9.2	8.7	15 year old	55.2	50.8	48.6	46.7
10 month old	10.2	9.1	9.5	8.9	16 year old	57.2	52.2	53.0	49.2
12 month old	10.4	9.9	9.9	9.6	17 year old	58.7	51.9	54.9	51.2
15 month old	10.8	10.1	10.5	9.8	18 year old	60.9	51.9	56.8	51.7
18 month old	11.7	11.0	11.0	10.4	19 year old	61.2	51.8	58.8	52.3
21 month old	12.4	11.6	11.7	11.1	20 year old	65.7	53.7	61.8	52.7
2 year old	13.5	12.7	12.8	11.9	30 year old	67.5	56.7	63.2	54.7
3 year old	16.0	15.4	14.3	13.8	40 year old	67.7	59.2	62.1	56.0
4 year old	17.8	17.0	16.0	15.5	50 year old	67.2	60.2	60.5	55.0
5 year old	19.7	19.0	17.7	17.1	60 year old	66.6	59.0	58.2	51.4
6 year old	22.2	21.1	19.4	18.7	70 year old	63.5	55.0	55.5	48.6
7 year old	24.8	23.2	21.7	20.6	80 year old	59.4	48.8	53.5	46.1
8 year old	27.2	26.0	23.9	22.9					

Table 6 Age distribution and sex ratio of Shenyang

Proportion of Different Gender in Total Population (%)		Different Ages of the Population (Thousand)					
		0–14 years old		15–59 years old		≥60 years old	
Male	Female	Urban	Rural	Urban	Rural	Urban	Rural
50.52	49.48	550	242	4754	1320	944	296

For adults, the overall risk in the region was not very high, and the city has acceptable levels of nitrate. However, the children's health risk was significantly higher than that of adults, and was unacceptable near the sewage irrigation area. Conversely, the children's risk was relatively low in the city.

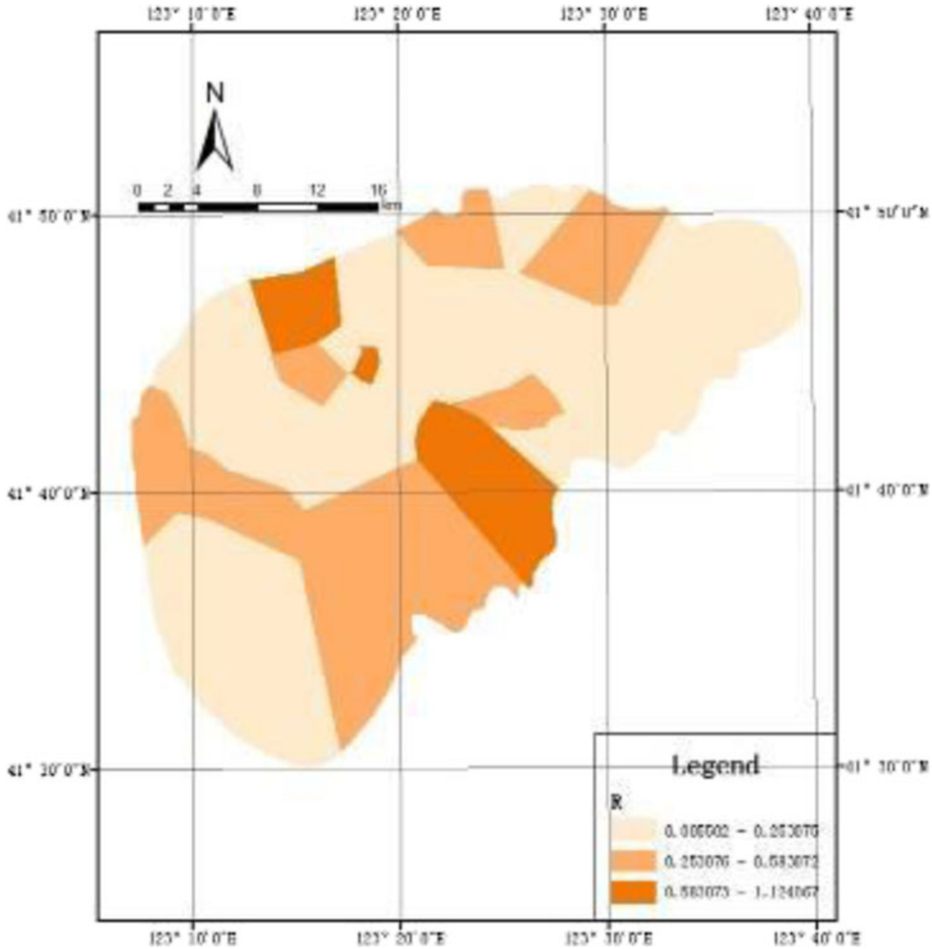

Fig. 2 Distribution of adult health risk

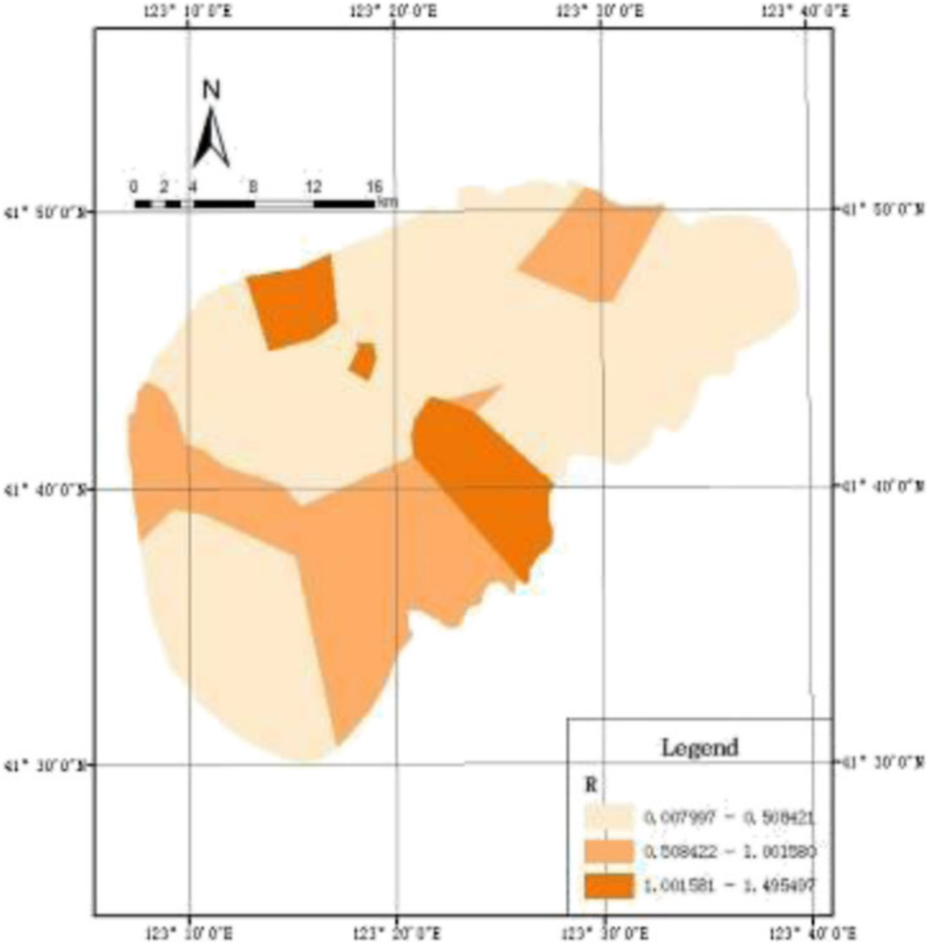

Fig. 3 Distribution of child health risk

3.2.5 Uncertainty Analysis

Risk assessment is always accompanied by uncertainty, and ignoring this uncertainty would result in managers of related sites receiving biased information, which would ultimately impact their decision-making process (Yang et al. 2010).

In this study, there were several sources of uncertainty. 1) Most of the values for parameters used were derived from the USEPA for other areas, which will reduce the accuracy of the model. Moreover, the seasonal changes in groundwater nitrate content were not considered in the model. 2) The health risk rating by the constraints of the receptor is strong because of uncertainty associated with the strong arbitrariness, different drinking habits and different sources of drinking water. 3) Uncertainties of the dose effect, the analysis using the standard EPA recommended values, but the different regions of the receptor is not the case, the standards of the dose effect also changes.

4 Conclusions and Recommendations

(1) Drinking groundwater contained high concentrations of nitrates harmful to human health in the study area, with nitrate being detected in 91.4 % of samples and at excessive levels in 34.3 % of the samples.
(2) The study area groundwater nitrate risk was higher near the sewage irrigation channels and agricultural areas, while less risk was observed in urban areas. In addition, adult health risk was less than that of children.
(3) The parameters used in the model were mostly obtained from the USEPA; therefore, additional studies are needed to generate data specific to the study area.

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