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Health risk assessment of nitrate pollution of drinking groundwater in rural areas of Suihua, China

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ABSTRACT

In order to investigate the health risks of NO_3^- in rural drinking groundwater in Suihua, China and provide a basis for healthy drinking water, 40 sets of groundwater samples were collected in the Suihua area, and the average concentration of nitrate in the study area was 71.66 mg/L, statistical analysis software (SPSS19), Hydrogeochemical Analysis Software (AqQA) and groundwater pollution analysis software were used. Through water sample collection, chemical analysis and construction of human health risk model (HHRA), a qualitative and quantitative assessment of NO_3^- health risk was carried out for people of different ages and sexes, and it was concluded that there was NO_3^- pollution health risk in rural drinking groundwater in Suihua. Health risk level: infants > children > adult females > adult males. The evaluation provides a scientific basis for the prevention and control of NO_3^- pollution in groundwater and new ideas for preventing human health risks.

Key words: China, drinking groundwater, groundwater quality, human health risk assessment, nitrate pollution

HIGHLIGHTS

- The study identified the distribution pattern of nitrate in rural drinking groundwater in the Suihua area, providing a basis for preventing excessive use of fertilizers and pesticides.
- The chemical characteristics of groundwater in the study area were reflected and described through the Durov plot.
- A HHRA was first constructed in the Suihua area to evaluate the level of health risk in the study area.

INTRODUCTION

Groundwater is one of the precious natural resources, and the amount of groundwater resources accounts for one-third of the total water resources. Groundwater is closely related to people's production and life (Alireza *et al.* 2020; Tian *et al.* 2020a). Groundwater is particularly important in areas with insufficient surface water resources (Zakhem & Hafez 2015; Tian *et al.* 2021). However, as the drinking water source of 70% of China's population, the groundwater has been polluted (Sun *et al.* 2020a, 2020b), and the shallow groundwater and deep groundwater polluted by nitrides, phosphates and heavy metal ions have reached 80 and 30%, respectively (Sun *et al.* 2020a, 2020b). Because groundwater pollution is highly hidden and difficult to detect, it is difficult to control the polluted groundwater (Li *et al.* 2016).

Nitrate (NO_3^-) pollution in groundwater is a worldwide environmental problem. Nitrate is easy to dissolve and has strong fluidity (Gu *et al.* 2013; Zhai *et al.* 2015; Tian *et al.* 2020b). It can enter underground through leaching and surface runoff (Li *et al.* 2015). It is a chemical pollutant that widely exists in groundwater (Hand *et al.* 2013; Sun *et al.* 2019). Drinking groundwater polluted by nitrate for a long time will lead to digestive system cancer, methemoglobinemia, blue baby syndrome and other diseases, posing a serious threat to human health (Han 2014; Sun *et al.* 2017; Chen *et al.* 2020). Nitrate-contaminated groundwater will cause harm to the human body when it enters the human body; therefore, it is necessary to evaluate the harm and degree of nitrate-contaminated groundwater. HHRA is a qualitative and quantitative assessment method for the hazard degree of polluted groundwater to the human body (Ni *et al.* 2010; Sun *et al.* 2022a, 2022b).

In 1983, the National Academy of Sciences (NAS) proposed for the first time a 'four-step method' based on hazard identification, dose-effect assessment, exposure assessment and risk characterization to assess the risks of environmental pollutants to human health. Then, the United States Environmental Protection Agency (USEPA) made a more detailed description of health risk assessment. At present, the 'four-step' health risk assessment model is applied to the health risk assessment of various pollutants in various environmental media. Saravanan *et al.* (2022) and Zhang *et al.* (2021) used models to evaluate the impact of high nitrate in groundwater on human health in different regions.

Suihua region is the main food production base in China. In order to increase agricultural production, farmers use nitrate fertilizers more frequently. In rural areas of this region, groundwater is the main source of drinking water. In order to scientifically prevent and control the health risks caused by excessive use of NO_3^- fertilizers in this region, the distribution pattern and pollution status of NO_3^- in this region are investigated, and the health risks of NO_3^- in drinking groundwater are evaluated. It is essential for the health of the rural population in the main agricultural production areas.

MATERIALS AND METHODS

Study area

The research area is located in the middle of Heilongjiang Province, China, with the geographical coordinates of 124°13′–128°30′E and 45°3′–48°02′N. The terrain inclines from northeast to southwest, and the overall landform is composed of four parts: low mountains and hills, Piedmont platform, low plain and flood plain. It is a continental climate with four distinct seasons. The average annual temperature is about 2.9 °C, the average annual sunshine time is 2,395 h, the average annual precipitation is 552.5 mm, the average annual evaporation is 1,337 mm and the average frost-free period is 140 days. The river network density in the study area is relatively large, belonging to the Songhua River system, and most of its areas are located in the Hulan River basin, the primary tributary of the Songhua River. The average annual total water resources of the city is 44.77×10^8 m^3. The stratum in the area mainly exposes Paleozoic carbonate, clastic rock and metamorphic volcanic rock, Mesozoic volcanic rock series, sedimentary rock series and Quaternary Holocene alluvial-proluvial layer. The main fault in this area is the Hulan River fault, which extends in the northeast direction. According to the occurrence conditions and hydraulic characteristics of groundwater, the groundwater in Suihua can be divided into three categories: Quaternary loose rock pore water, Cretaceous loose rock pore fissure water and bedrock fissure water. Infiltration recharge of atmospheric precipitation is one of the recharge sources of groundwater. The runoff and discharge of groundwater are mainly affected by the characteristics of aquifers, and then by topography, geomorphology, geological structure, characteristics of aeration zone and other factors.

Sampling and measurements

The sampling points are evenly distributed in the work area, with the principle that each point represents different regions and soil types, and the sampling time is August 2022. A total of 40 groups of groundwater samples were collected (Figure 1). The water samples are collected, stored and sent in strict accordance with the Technical Specifications for Groundwater Environmental Monitoring (H/164-2004).

No. 1 plastic bottle, volume 2.5 L, analysis types: TDS, CO_2, $CaCO_3$, H_2SiO_3, Li^+, Na^+, NH_4^+, F^-, Cl^-, NO_3^-, SO_4^{2-}, stored at room temperature; No. 2 plastic bottle, with a volume of 500 ml. Analysis types: Cr, Fe, Li, Mn, Ni, Sr. Add 2–3 ml HNO_3 (1:1) protective agent and store at room temperature; No. 3 plastic bottle, volume 250 ml, analysis type: Se, As, with 1 ml HCl (1:1) protective agent added, stored at room temperature; No. 4 brown glass bottle, volume 250 ml, analysis type: Hg, with 8–10 ml of protective agent (5% nitric acid as a solvent, potassium dichromate concentration is 0.5 g/L) added, and stored at 4 °C at constant temperature, and sent to the laboratory within 24 h. The water sample testing was completed by the Harbin Natural Resources Comprehensive Survey Center Laboratory of the China Geological Survey.

The measurement method for TDS is the gravimetric method, which uses instruments and equipment such as a balance, oven and evaporating dish. CO_2 and $CaCO_3$ are measured using the titration method using instruments and equipment such as burets and triangular flasks. The determination method of H_2SiO_3 is silicon molybdenum yellow spectrophotometry, using instruments and equipment such as a spectrophotometer and a colorimetric cup. The determination method for F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, Li and NH_4^+ is ion chromatography (IC), using instruments and equipment such as IC, cation protection and separation columns, and cation inhibition columns. The determination method of Cr is the catalytic polarographic method, using instruments and equipment such as a polarograph and an exchange column. The method for measuring Hg is cold atomic absorption spectrophotometry, which uses instruments and equipment

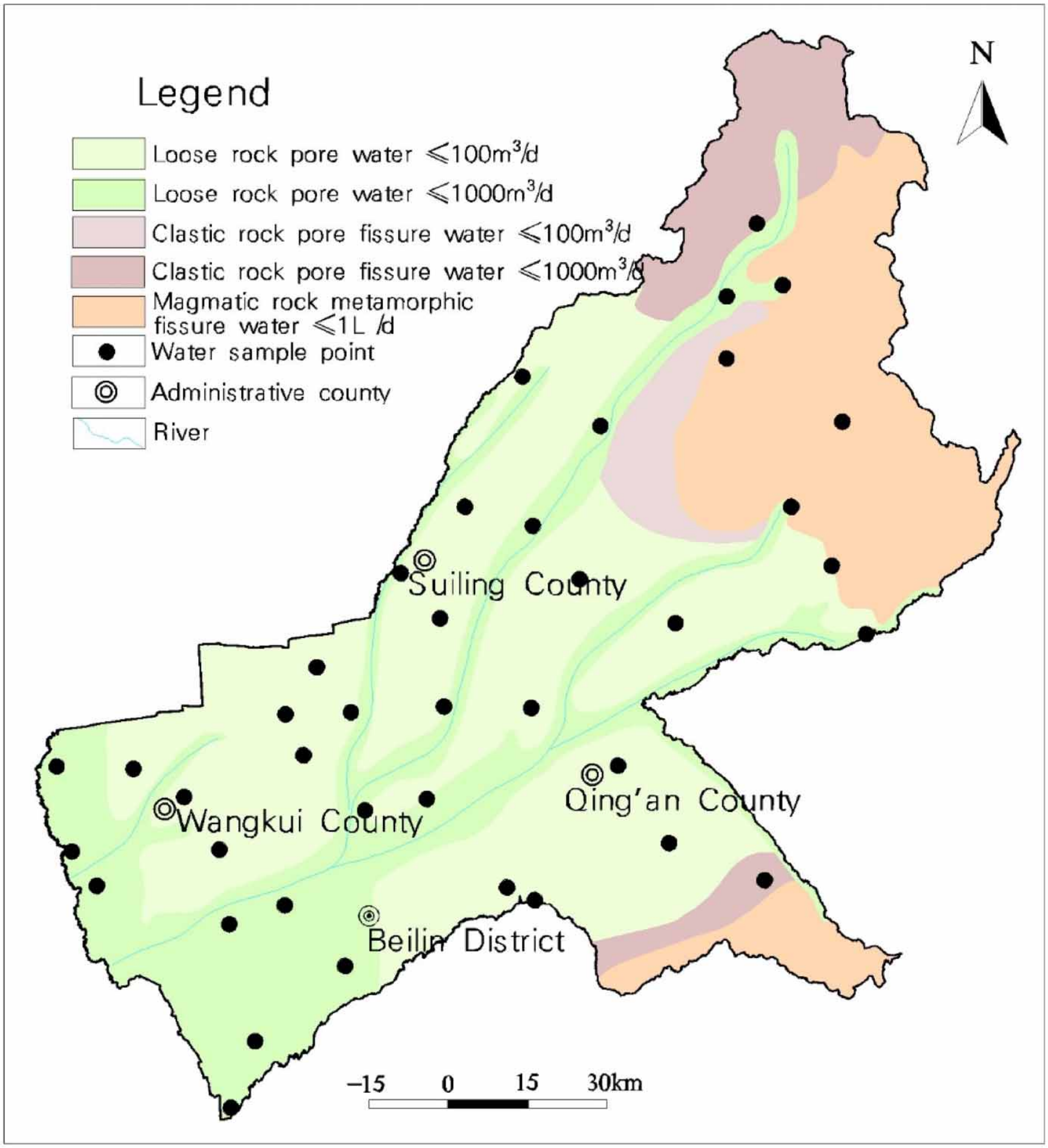

Figure 1 | Distribution of sampling points.

such as an atomic absorption spectrophotometer and its mercury measuring accessories or instruments, a mercury hollow cathode lamp and a mercury absorption cell. The determination method for Fe, Mn and Sr is by inductively coupled plasma atomic emission spectroscopy, using an instrument and equipment called an inductively coupled plasma atomic emission spectrometer. The determination method of As is hydride generation atomic fluorescence spectroscopy, using instruments and equipment such as an atomic fluorescence spectrometer, an arsenic special hollow cathode lamp, and a steel cylinder argon (purity ≥ 99.99%). The method for determining Se content is the catalytic polarographic method, which uses instruments and equipment such as a polarograph and a three electrode system (drop mercury, silver or calomel electrode and platinum wire).

The water sample test shall be completed by a testing unit with national testing qualification. Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} were determined by ICP-OES, Cl^{-} and SO_4^{2-} were determined by IC, H_2SiO_3 was determined by ultraviolet spectrophotometry (UV), total dissolved solids (TDS) was determined by gravimetric method (GR) and HCO_3^{-} was determined by volumetric method (VOL).

The reliability test of the water sample data is carried out by using the anion and cation balance test methods, and the absolute value of the relative error *E* of the anion and cation balance is less than 5% as the reliable data. After the test, all data are reliable data.

Human health risk assessment model and parameter acquisition

The groundwater quality health risk assessment is an effective method to quantitatively evaluate the hazard degree of hazardous substances in groundwater to the human body. Generally, the assessment starts with hazard identification and then carries out a dose-effect analysis to evaluate exposure and risk characterization (Zhou *et al.* 2016; Tian *et al.* 2020c). On the basis of field investigation, sampling and indoor analysis (hazard determination), combined with the information on the harmful effects of chemicals on human health provided by the International Center for Research on Cancer (IARC), determine the health effects of nitrate on humans (dose-effect relationship) (Chen 2010; Chen *et al.* 2016).

At present, there are many risk models for evaluating the hazards of groundwater pollutants to human beings, among which the HHRA model recommended by the USEPA (Chen *et al.* 2017; Zhai *et al.* 2017; Javaid *et al.* 2019) is the most widely used in the groundwater pollutant risk assessment (Su *et al.* 2013; Zhang *et al.* 2017; Mahmoud *et al.* 2018). In this paper, the health risk caused by nitrate pollution in groundwater in the Suihua area is scientifically evaluated by using the evaluation model.

Hazard identification

The first step in HHRA is to identify hazards, that is, to determine the potential adverse effects of human intake of hazards, the possibility of such adverse effects and the certainty and uncertainty of such adverse effects. The objective is to evaluate the evidence weight of adverse health effects according to the evaluation results of all existing toxicity and action mode data.

In order to achieve this goal, more detailed site-related data and historical information are needed; Concentration data of pollutants in site groundwater and other samples; Analysis data of physical and chemical properties of the site; Climate, hydrological and geological characteristics information and data of the site (location); Relevant information such as land use mode, sensitive people and buildings of the site and surrounding plots.

Dose-response assessment

The four-step model of population health risk assessment of the USEPA defines the dose-response assessment as 'describing the possibility and severity of adverse health effects under a certain exposure dose and exposure conditions of a chemical substance'. The dose-response relationship assessment provides a mathematical basis for converting exposure information to assess the health risk. The dose-response relationship can be expressed by reference dose (RfD) (USEPA 2005). The determination of RfD is as follows:

$$\mathrm{RfD} = \frac{\mathrm{NOAEL(LOCAEL)}}{\mathrm{UFs}} \tag{1}$$

The symbols represent the following meanings: RfD – chronic reference dose (mg/kg/d); LOCAEL – lowest observed adverse effect level (mg/kg/d); NOAEL – no adverse effect level observed (mg/kg/d); UFs – Uncertainties.

The acceptable standard value for nitrate concentration is 10 mg/L (USEPA 2001; Yang *et al.* 2012).

Exposure assessment

Exposure assessment is a process of measuring, estimating or predicting the intensity, time and frequency of people's exposure to pollutants in the medium. The exposure assessment is the quantitative basis for risk assessment, which is mainly the assessment of exposure environment, environmental concentration, receptor exposure route, environmental medium and exposure.

According to the definition of USEPA, skin absorption, air inhalation and direct drinking water intake were originally considered in the groundwater health risk assessment model. Since the nitrogen in groundwater does not volatilize, this paper only considers drinking water intake and skin intake, not air inhalation. Its calculation formula is:

$$I_{CDI} = \frac{C \times IR \times ABS \times EF \times ED}{BW \times AT} \quad (2)$$

$$I_{CDD} = \frac{C \times SA \times Kp \times EV \times ET \times EF \times ED \times CF}{BW \times AT} \quad (3)$$

The meanings of the parameters in the above two equations are as follows: I_{CDI} denotes the daily average exposure dose through drinking water (mg/kg/d); I_{CDD} denotes the daily average exposure dose of skin contact route (mg/kg/d) and C is the measured concentration of nitrate in groundwater (mg/L).

The meanings of other parameters are shown in Table 1.

Risk characterization

Risk characterization is a process to estimate the probability of adverse health reactions of people exposed to target pollutants under various conditions. It is the last step of risk assessment. In this step, the data and analysis of the first three steps are integrated to estimate and predict the probability of response to the health effects of the exposed population caused by groundwater nitrate pollutants or the probability of the expected hazard level (Dzulfakar *et al.* 2011; Huang *et al.* 2018). It can be expressed as:

$$HI_{oral-water} = \frac{I_{CDI}}{RfD_{oral-water}} \quad (4)$$

$$HI_{derm-water} = \frac{I_{CDD}}{RfD_{derm-water}} \quad (5)$$

$$HI = HI_{oral-water} + HI_{derm-water} \quad (6)$$

In the above three formulas, each parameter represents the following meanings: $HI_{oral-water}$ is the non-carcinogenic oral hazard coefficient (dimensionless); $HI_{derm-water}$ is the non-carcinogenic skin hazard coefficient (dimensionless); $RfD_{oral-water}$ is the reference dose of drinking water (mg/kg/d), taken as 1.6; $RfD_{derm-water}$ is the reference dose absorbed

Table 1 | Meaning and value of each parameter

Parameter meaning		Value				Unit
		Children	Females	Males	Infants	
EF	Exposure frequency	365	365	365[b]	365	d/a
BW	Average body weight	32.02[a]	60.4[a]	69.55[a]	7.68[a]	kg
ABS	Gastrointestinal absorption coefficient	0.5[c]	0.5[c]	0.5[c]	0.5[c]	
IR	Amount of drinking water	1.5[b]	2[e]	2[e]	0.65[b]	L/d
ED	Exposure duration	6[b]	30[b]	30[b]	0.5[d]	a
SA	Body surface areas	9,035.2	1,600[a]	1,700[a]	3,416	cm^2
AT	Average exposure time	2,190	10,950	10,950	182.5[b]	d
EV	Bathing frequency	1[b]				time/d
ET	Bath time	0.167[c]				h/d
CF	Unit conversion factor	0.002[b]				L/cm^3
Kp	Dermal adsorption	0.001[b]				cm/h

[a]These data come from PRCMH (2003).
[b]These data come from USEPA (1989).
[c]These data come from USEPA (1991).
[d]These data come from USEPA (2004).
[e]These data come from Tian *et al.* (2020d).

by skin (mg/kg/d), taken as 1.0; I_{CDI} is the intake dose of drinking water (mg/kg/d); I_{CDD} is the skin absorbed dose (mg/kg/d) and HI is the total risk coefficient (dimensionless).

For the groundwater risk control value based on the non-carcinogenic effect, the non-carcinogenic risk threshold recommended by USEPA is 1 (Huang *et al.* 2017; Wu *et al.* 2018; Javed *et al.* 2019).

In order to provide targeted and effective protection according to different groups of people, this paper carries out NO_3^- risk assessment for infants (1 year old and below), children (2–17 years old), adult males and adult females, respectively (see Table 1 for specific parameters).

Data analysis

The distribution of groundwater chemical concentration and the correlation of its components were analyzed by SPSS 19. This method reveals the correlation between different chemical components of groundwater.

Water quality analysis

The quality standard for groundwater of the People's Republic of China is adopted for evaluation (GB/T14848-2017) (QSGC).

For the comprehensive evaluation of groundwater quality, the scoring method with notes is used to evaluate the individual components of the participating projects, divide the levels of the components, and determine the evaluation score F_i of the individual components, respectively, according to the standards in Table 2, the formula for calculating the F-value of the comprehensive evaluation score is as follows:

$$F = \sqrt{F_{\text{avg}}^2 + F_{\max}^2} \quad (7)$$

where $F_{\text{avg}} = \sum F_i/N$ is the average value of evaluation score F_i of each single component; $F_{\max}$ is the maximum value in the evaluation score F_i of single component and N is the number of participating projects.

Then, according to the F-value, the groundwater quality is classified according to the method specified in the standard (see Table 3).

RESULTS AND DISCUSSION

Distribution characteristics of substances in groundwater

The minimum, maximum, average, standard deviation and coefficient of variation of substances in groundwater were statistically analyzed using SPSS software. The size of the coefficient of variation showed the uniformity of substance distribution. The smaller the coefficient of variation, the more uniform the substance distribution was. The larger the coefficient of variation, the more uneven the substance distribution was. The distribution characteristics of substances in the study area are shown in Table 4.

In order to more intuitively reflect the distribution characteristics of the original data and compare the distribution characteristics of multiple sets of data, a box diagram of each substance was drawn, from which it can be seen that the distribution of

Table 2 | Quality evaluation and grading of a single component

Category	I	II	III	IV	V
F_i	0	1	3	6	10

Table 3 | Classification of a comprehensive evaluation of groundwater quality

Code	I	II	III	IV	V
Level	Excellent	Good	Preferably	Poor	Range
Pollution degree	Uncontaminated	Slight pollution	Medium pollution	Heavy pollution	Severe pollution
F	$F < 0.80$	$0.80 \leq F < 2.50$	$2.50 \leq F < 4.25$	$4.25 \leq F < 7.20$	$F \geq 7.20$

Table 4 | Statistical table of groundwater indicators (pH: dimensionless, other indicators in mg/L)

	Minimum value	Maximum value	Average	Standard deviation	Coefficient of variation
pH	5.75	9.12	6.81	0.72	0.11
TH	0.00	898.72	230.73	225.01	0.98
H_2SiO_3	2.17	38.90	18.72	9.68	0.52
CO_2	0.00	104.28	41.51	22.50	0.54
Li^+	0.00	0.11	0.02	0.03	2.03
TDS	3.71	1,560.00	504.81	367.69	0.73
Sr	0.02	1.13	0.48	0.33	0.70
Se	0.0000	0.0015	0.0001	0.0002	4.3053
Ni	0.00	0.03	0.00	0.00	6.32
As	0.0000	0.0089	0.0012	0.0025	2.1057
Hg	0.000000	0.000090	0.000014	0.000025	1.832122
Cr	0.00	0.03	0.00	0.01	6.32
Mn	0.00	4.71	0.71	1.00	1.42
Fe	0.02	15.03	1.57	3.11	1.98
Na^+	0.33	153.81	44.11	35.54	0.81
NH_4^+	0.00	0.91	0.18	0.24	1.36
F^-	0.00	5.79	0.35	0.93	2.64
Cl^-	1.70	240.65	52.93	55.99	1.06
NO_3^-	0.00	599.66	71.66	125.56	1.75
SO_4^{2-}	1.08	330.37	79.48	91.97	1.16

each substance in the study area is different (Figure 2). The average concentration order of the analytical elements is TDS $>$ TH $>$ SO_4^{2-} $>$ NO_3^- $>$ Cl^- $>$ Na^+ $>$ H_2SiO_3 $>$ pH $>$ DO $>$ Fe $>$ CO_3^{2-} $>$ Mn $>$ Sr $>$ F^- $>$ NH_4^+ $>$ Li^+ $>$ As $>$ Cr $>$ Ni $>$ Se $>$ Hg. Their different concentrations reflect the distribution of the sample points.

Chemical type of groundwater

The Durov map drawn by AqQA software is used to reflect and describe the chemical characteristics of groundwater in the study area (Sun *et al.* 2021, 2022a, 2022b). The chemical difference between anions and cations in groundwater is shown in Figure 3. Most of the cations in the groundwater fall in the calcium type area, some in the mixed type area and a few in the sodium type area, mainly in the calcium type area, while the majority of the anions fall in the bicarbonate type area and mixed type area, and a few in the sulfate type and chloride type area. It shows that the groundwater in the study area is mainly calcium type water, and the different areas are sulfuric acid type, chloride type, bicarbonate type and mixed type. The pH value of the groundwater sample is 5.5–9.5, and the TDS concentration of the sample is 0–1,600 mg/L. The letters in the figure represent different sample points.

Groundwater quality assessment

After calculation, the single index evaluation result of groundwater is shown in Figure 4.

It can be seen from Figure 4 that the single index evaluation of groundwater quality in the study area is generally good, most of the indicators meet the Class I water standard, the vast majority of indicators are in Classes I–III, and only six indicators meet the Class V water quality standard, namely: Fe, Mn, NO_3^-, $CaCO_3$, F^-, pH, the order of exceeding the standard and the size of exceeding the standard are Fe $>$ Mn $>$ NO_3^- $>$ $CaCO_3$ $>$ F^- $>$ pH, 21.95, 17.07, 17.06, 7.32, 4.88 and 2.44%. There are four indicators that meet the Class IV water quality standard, namely TDS, SO_4^{2-}, NH_4^+ and Ni. The order and ratio of exceeding the standard are: TDS $>$ SO_4^{2-} $>$ NH_4^+ $>$ Ni, 12.20, 9.76, 7.32 and 2.44%.

According to the comprehensive evaluation results, the groundwater quality classification map (Figure 5) is prepared.

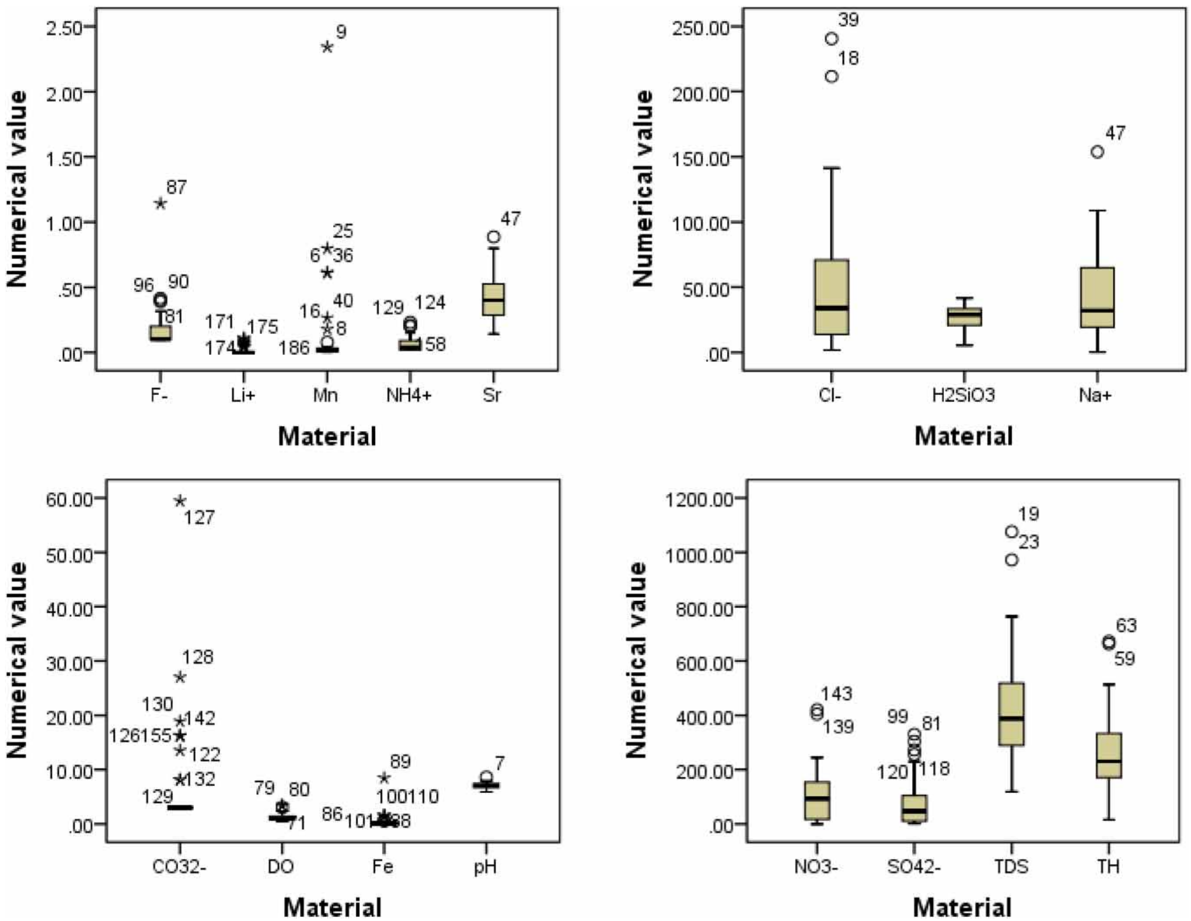

Figure 2 | Chemical concentration distribution map of groundwater (pH: dimensionless, other material units: mg/L).

According to the calculation results, the quality of groundwater in the area can be divided into four levels, of which Class III water does not. In general, the quality of groundwater is worrying. Class I water accounts for 2%, Class II water accounts for 5%, Class IV water and Class V water account for 93%, of which Class IV water accounts for 71% and Class V water accounts for 22%. Classes IV and V water are greatly affected by human activities, especially the use of NO_3 fertilizers in agricultural production.

Nitrate pollution of groundwater

The test results show that the minimum value of NO_3^- is 0, the maximum value is 599.66, the average value is 71.66 and the coefficient of variation is 1.75. It can be seen that the variation characteristics of NO_3^- are obvious, and the distribution differences are large. Figure 6 shows that NO_3^- Class I area accounts for 48.05% of the sample data, Class II area accounts for 10.39% of the sample data, Class III area accounts for 16.88% of the sample data, Classes I and II water are mainly distributed in Suiling County – Changshan Town – Nierhe Township – Fazhan Township – Ping'an Town, Hongqi Manchu Township – Changfa Town, Class IV area accounts for 9.09% of the sample data, mainly distributed in the northeast of Suiling County and Class V area accounts for 15.58% of the sample data, mainly distributed in Wangkui Beilin and Qing'an, as well as the central area of Suiling.

The results show that the nitrate pollution degree of groundwater in this area is relatively high, with zoning. In general, the over-standard rate of NO_3^- is 24.67%, and the high content of NO_3^- cannot be ignored, and a health risk assessment is required.

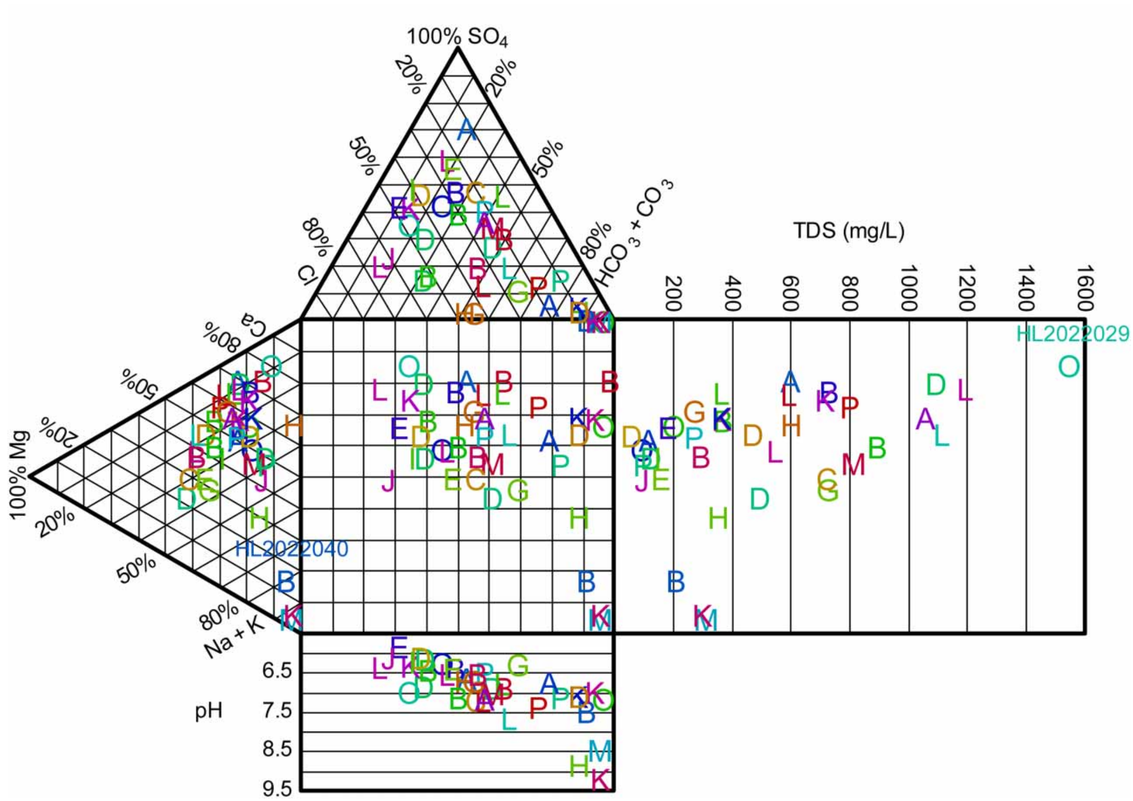

Figure 3 | Durov diagram of hydrochemistry in the study area.

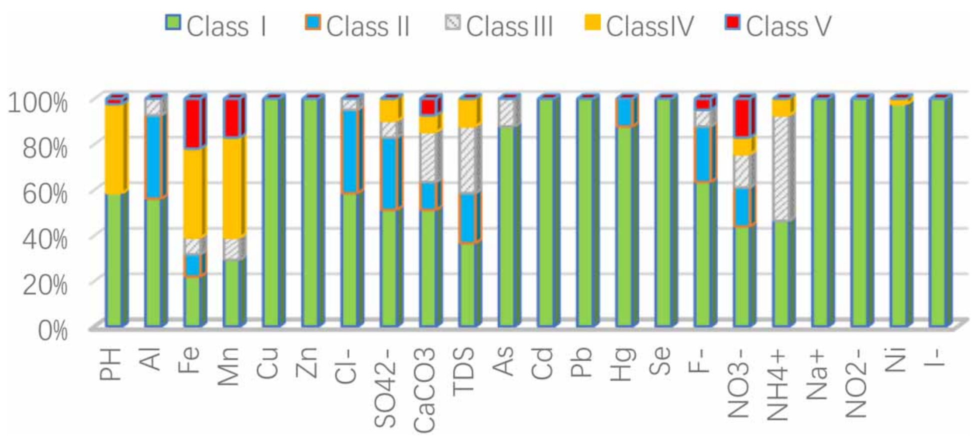

Figure 4 | Water quality accumulation histogram of the single index of groundwater.

Health risk assessment

Through the evaluation, the health risk assessment chart (Figure 7) is prepared. It can be seen from Figure 7 that NO_3^- pollution has health risks, and the main risk areas are concentrated in Wangkui, Beilin and Qing'an. The results showed that the risk of NO_3^- pollution in groundwater in the study area to adults was smaller than that of children and infants. However, about 30% of the study area belonged to the health risk area.

The adult female hazard zone ($HI > 1$) roughly overlaps with the male hazard zone. This finding is consistent with the findings in the Weining Plain in northwest China. There are differences in the health risks of NO_3^- pollution to different sex groups, and it emphasizes the importance of gender in the HHRA process.

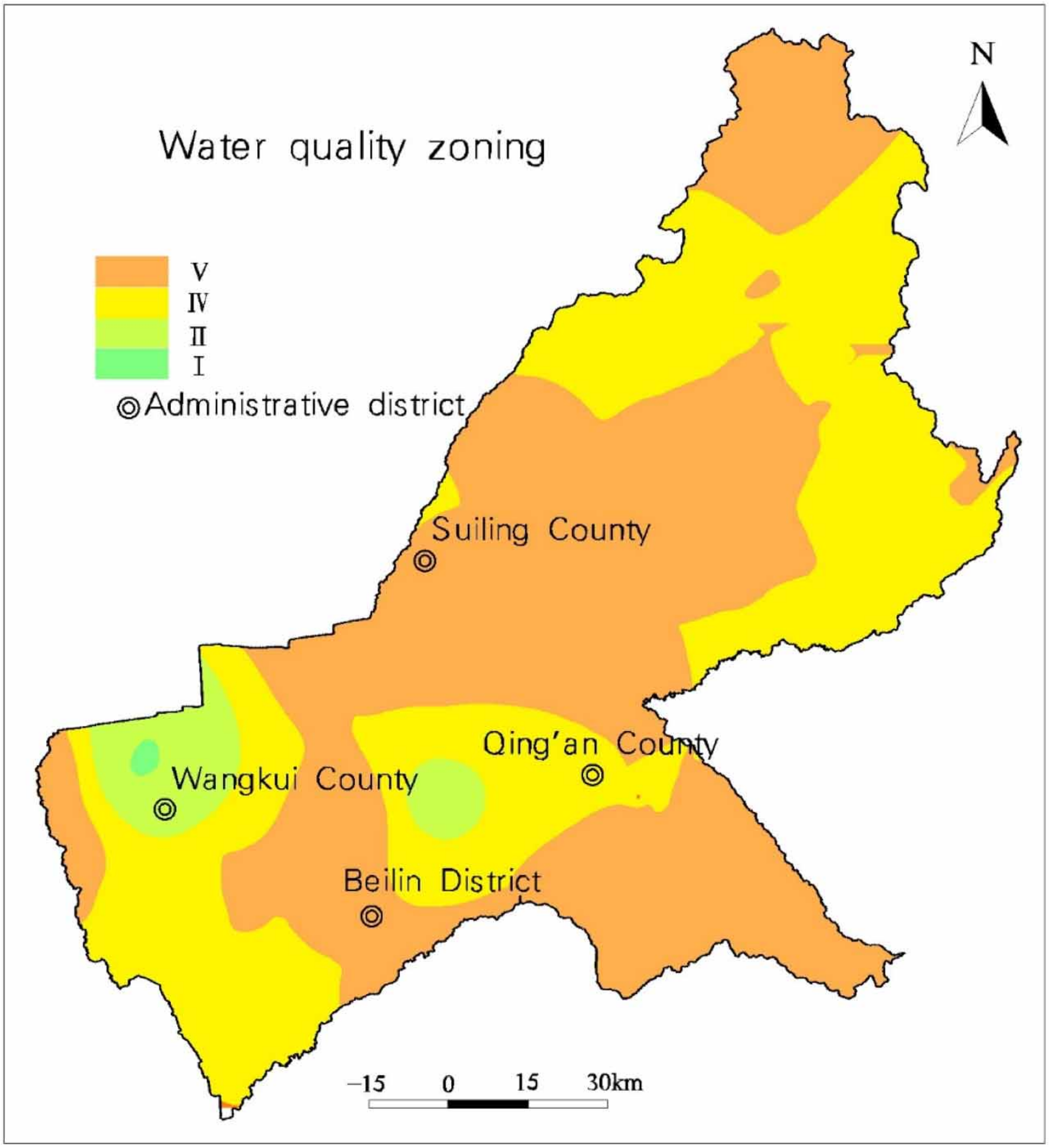

Figure 5 | Spatial distribution of groundwater quality.

The health risk area of children is larger than that of adults. About 37.5% of the study area belongs to the child health risk area, and the infant health risk area is the largest. About 45% of the area belongs to the infant health risk area, which is distributed in Wangkui County, Beilin District, Qing'an County and the northeast of Suiling County.

The results of the HHRA health risk assessment are shown in Figure 8. The maximum HI value of adult male is 10.81, and the average value is 1.29; The maximum HI value of adult women is 12.45, and the average value is 1.48; The maximum HI value of children is 17.98, and the average value is 2.14; The maximum HI value of infants is 32.03, and the average value is 3.83. It can be seen that the health risks of adult men and adult women are different. The health risks of adult women are higher than those of adult men, but the difference is not significant. The health risks of adults are lower than those of children and infants, and the health risks of infants are the largest, that is, infants > children > adult women > adult men, and the risk of men is higher than that of women, which is related to the differences in the weight of different age groups. The risk close to the urban area is lower than that in the rural area, mainly due to the

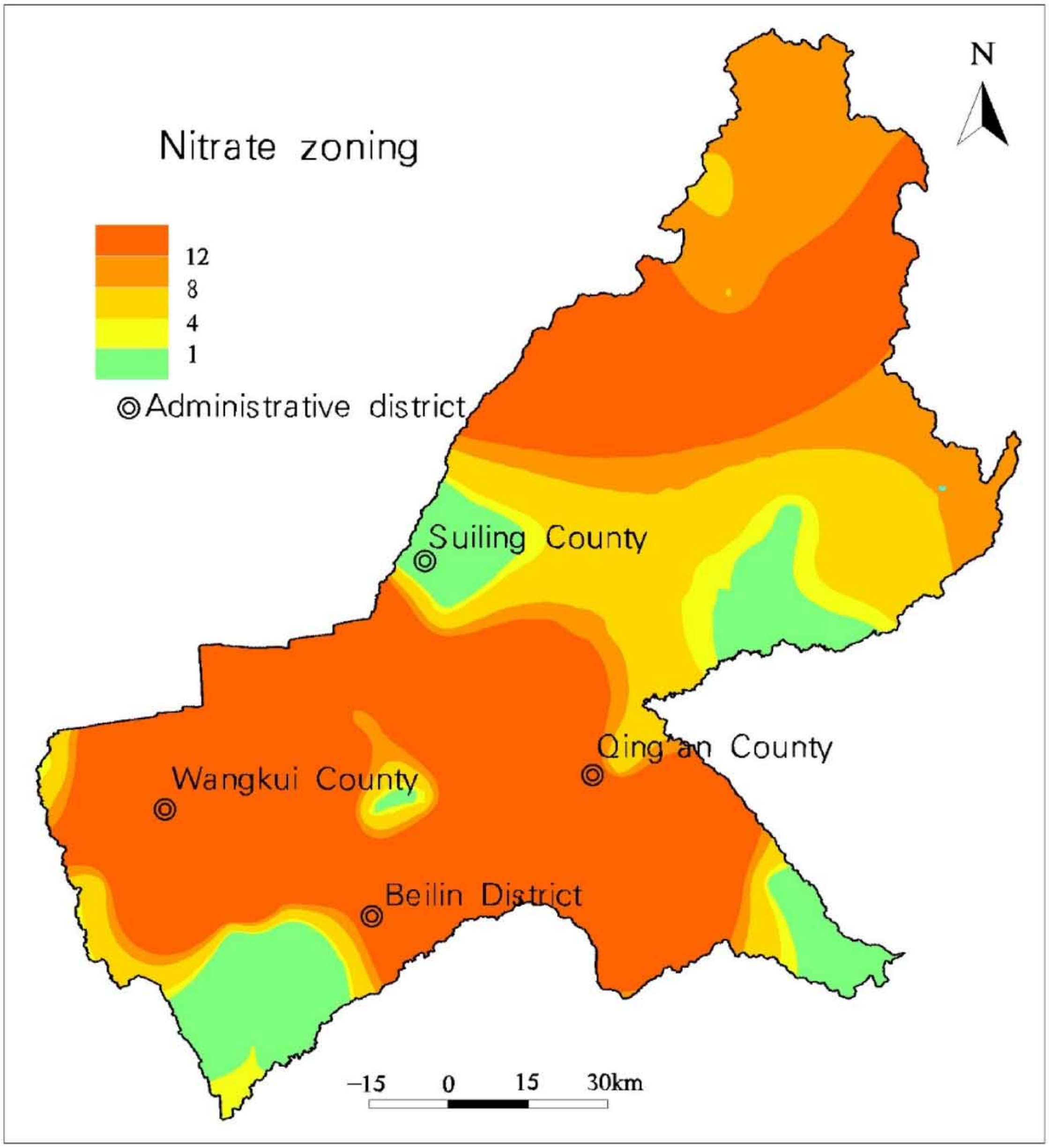

Figure 6 | Nitrate pollution zoning map.

use of NO_3^- fertilizer and organic fertilizer in the rural area, while the urban area is not affected by NO_3^- fertilizer and organic fertilizer.

The risk results of drinking water intake and skin intake are shown in Figure 9. The risk of drinking water intake is significantly greater than that of skin intake. The proportion range of drinking water intake risk and skin intake risk is 41.5–312.5 times. Drinking water intake is the main way to cause health risks.

DISCUSSION

It can be seen from Figures 1, 5 and 6 that in the plain area where the pore water of loose rock is distributed, agricultural production activities are relatively developed and the amount of fertilizer used in farmland is large (Amir *et al.* 2021)

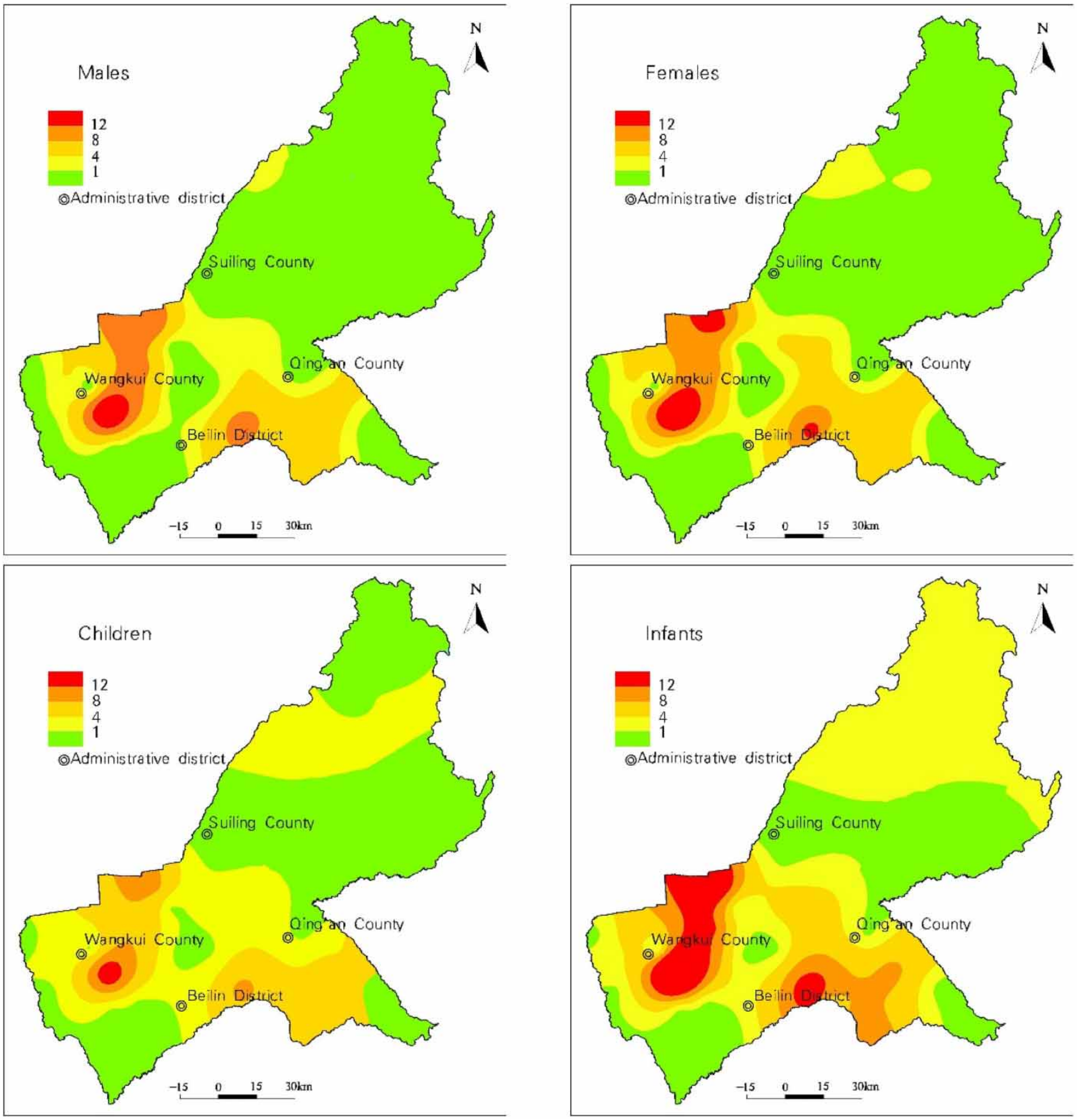

Figure 7 | Groundwater nitrate health risk assessment zoning map.

After farmland irrigation or rainfall, most of the water, except for partial evaporation and absorption by plants, seeps into the aeration zone or groundwater. The nitrogen components contained in fertilizer will gradually enter the groundwater environment with the infiltration of groundwater, resulting in nitrate pollution in groundwater (Anju & Kavita 2022). Therefore, compared with the mountainous areas with higher altitude and larger topographic gradient, the groundwater in the alluvial-proluvial plain areas with lower altitude and smaller topographic gradient is more vulnerable to agricultural non-point source pollution (Nitika *et al.* 2021).

Agricultural non-point source pollution leads to the continuous accumulation of nitrate in groundwater, and high nitrate concentration will cause serious harm to human health. Hypermethemoglobinemia is a health problem caused by high nitrate in drinking water. When the nitrate content is high in the body of newborns, cyanosis will also occur, which will lead to

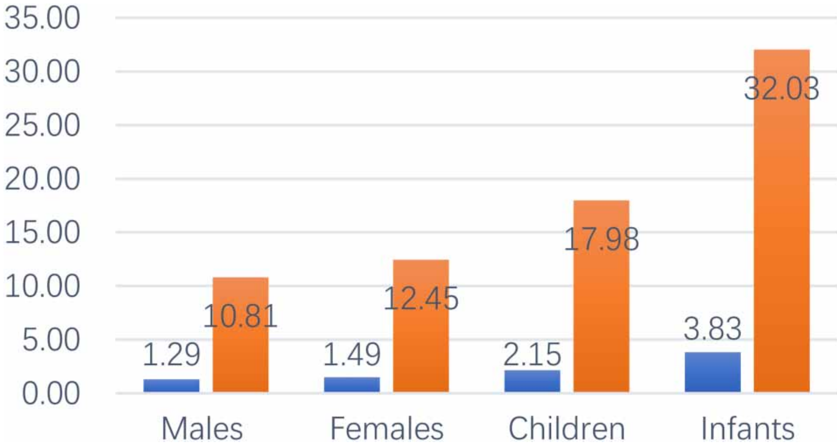

Figure 8 | Risk comparison chart of different age and gender groups.

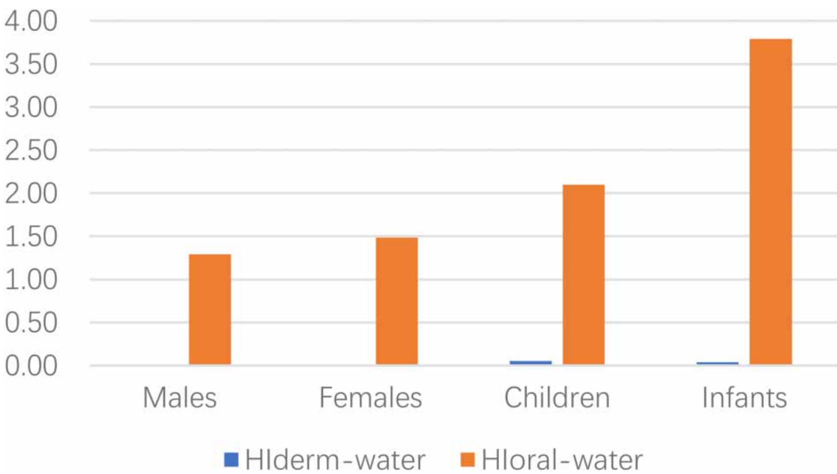

Figure 9 | Comparison of health risks of different populations and different intake routes.

mucous membrane blueness and digestive and respiratory diseases in infants (Marghade *et al.* 2021). The intake of large amounts of nitrate has a complex relationship with cancer, adverse reproductive outcomes and other health problems, which requires further research in the future. In this paper, the health risk assessment of adult men, adult women, children and infants is carried out, respectively, and the corresponding conclusions are drawn, which is conducive to improving people's awareness of the protection of infants and children against nitrate risk.

Du *et al.* (2022) identified and analyzed the nitrogen source of groundwater in the Beilin area of Suihua Basin based on isotope methods, and concluded that the high concentration areas of groundwater NO_3^- are mainly affected by agricultural activities and the infiltration of sewage discharge from upstream urban areas. Tian *et al.* (2020c) conducted a study on the health risks of groundwater chemistry and nitrate intake in Helen City, and found that human activities are the cause of the formation of chemical composition in shallow groundwater in Helen. The degree of harm caused by NO_3^- pollution is in the order of infants > children > adult females > adult males. The above two conclusions are consistent with this study, and the research results can provide technical reference and theoretical support for the evaluation of groundwater nitrate under the same type of hydrogeological conditions.

CONCLUSION

By analyzing the chemical characteristics, material distribution characteristics, nitrate pollution characteristics and quality characteristics of groundwater, an HHRA was constructed to evaluate the health risks caused by nitrate in groundwater. Scientific conclusions were drawn.

1. The groundwater in the research area is severely polluted by nitrate, which is mainly concentrated in the main human activity areas, especially in the main agricultural production areas.
2. The groundwater quality in the research area is relatively poor, partly due to the excessive use of nitrate-containing fertilizers and organic fertilizers in agricultural production.
3. NO_3^- pollution in groundwater poses a health risk to humans. There are significant differences in the health hazards of groundwater NO_3^- pollution in different genders and age groups, with the order of risk being infants $>$ children $>$ adult women $>$ adult men.
4. It is recommended to scientifically use nitrate fertilizers in agricultural production to reduce nitrate pollution. The research results provide a basis for preventing human health risks.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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