Nitrate source analysis of underground drinking water sources in Zhangjiakou main urban area and its health risk assessment

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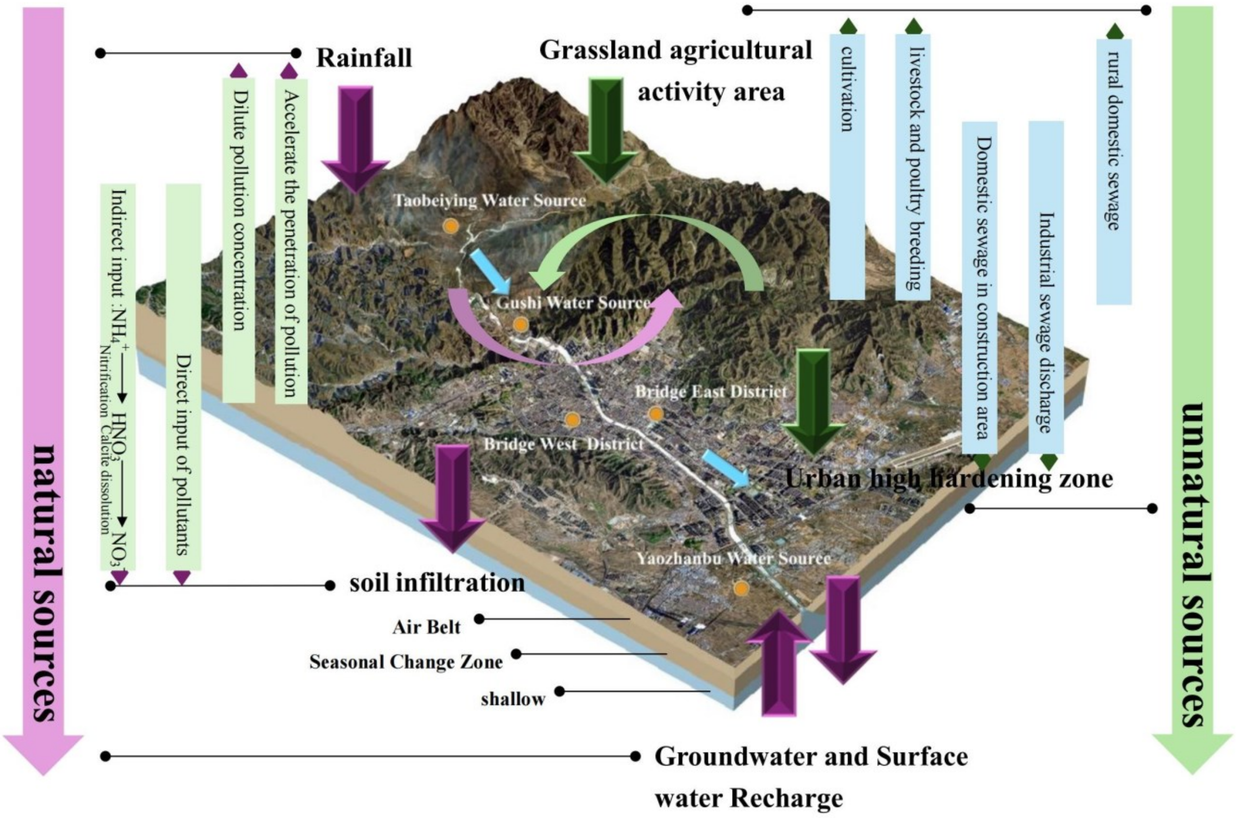
GRAPHICAL ABSTRACT



ABSTRACT

In order to investigate the main pollution factors of underground drinking water sources in semi-arid agricultural areas in China, and to reveal the threatening influence of pollutants on the normal water security of local society. Single-factor evaluation index, principal component analysis, basic data statistics are used to clarify the main pollution indicators of underground drinking water sources in Zhangjiakou main city and discuss the main influencing factors of the change of their pollution concentration, and evaluate the degree of health threat of its pollution to the drinking water of local residents. The results show that: the water sources of Taobeiying and Gushi are deeply affected by human activities, and nitrate, as the only exceeding substance under drinking water standards, is the most important indicator of groundwater pollution; and the nitrate con-centration of groundwater is higher in the pasture and nearby agricultural activities; nitrate contamination levels in groundwater are within the health acceptability range for the vast majority of the population, with only newborns in the Taobeiying drinking water source being exposed to a non-carcinogenic risk of nitrate. The results of the study will help to maintain a stable groundwater environment.

Keywords: groundwater contaminants, nitrate contamination, land use, agricultural activities, human health risk assessment

1. Introduction

Groundwater, as an important component of the Earth's water resources, provides all or part of the drinking water for up to 50 percent of the world's population(IGRAC, 2018, Project, 2023). Especially in arid and semi-arid areas where surface water resources are limited, groundwater has become the most important source of drinking water for the continuation of normal human life activities. The main city of Zhangjiakou is located in the transition zone of forest and grassland in northern China, and shoulders the important responsibility of water conservation and stabilizing the ecological environment. The city's water supply is highly dependent on groundwater resources. Along with climate change and economic growth, the amount of groundwater extracted has risen year after year, but recharge has been limited, so that by 2023, the underground water supply will account for 68.41% of the total water supply, with agriculture being the main source of water consumption, which will account for 66.39% of the total(Jasechko and Perrone, 2021, Province, 2023). The non-sustainable development of groundwater resources exposes them to problems such as restricted water circulation and pollution of the natural water environment, which in turn threaten human health and industrial development(Castellazzi et al., 2016). Therefore, elaborating the current status of groundwater environmental pollution in the region and evaluating the health risk of residents' drinking water will provide risk warning and scientific reference for maintaining the safety of drinking water for citizens in the main urban area of Zhangjiakou and the stability of the overall water environment.

Nitrate pollution is a common problem in the groundwater environment, which faces problems such as difficult to manage the contamination of water bodies and weak resistance of the water environment to damage due to the hydraulic cycle flow characteristics of groundwater(Benes et al., 1989). In recent years, the problem of groundwater nitrate pollution has become increasingly prominent in North China, especially in rural areas where groundwater is used as a source of drinking water(Hu et al., 2005). According to Gan et al(Gan et al., 2022), who studied the distribution, sources and health risks of nitrate in groundwater in the northern plains of China, it is clear that intensive groundwater mining has been identified as a key factor in exacerbating nitrate contamination, as the thicker envelope resulting from over-exploitation promotes the nitrification process. In addition, Chen et al(Chen et al., 2010) clarified the significant impact of wastewater irrigation on groundwater nitrate concentration levels based on analyzing the effects of land use changes and irrigation practices on nitrate pollution in shallow groundwater. In summary, the changes of nitrate levels in groundwater in North China are closely related to agricultural activities and groundwater resource management.

The undue attention to nitrate research stems from its harmful effects in the environment and in humans. First of all, excessive intake of nitrate from drinking water combined with microorganisms is converted into nitrite, which induces human methemoglobinemia, hypertension and cardiac system diseases, and so on, seriously endangering human health(Ebdrup et al., 2022, Lin et al., 2023); in addition, the excess of nitrate in the water will also be a burden on the carrying capacity of the aquatic ecosystem, which will lead to the occurrence of eutrophication in the water body, resulting in an imbalance of the aquatic ecosystem. Natural water bodies as a source of tap water, purification of nitrate is difficult to remove, even in trace amounts, when repeated boiling when the conversion of nitrite is able to pose a hazard to the human body(Hughes and Marion, 2021, Severe et al., 2023). With the development and popularization of contemporary hygiene and metrology, the impact of nitrate on human health has been quantified, thus this paper introduces the Human Health Risk Assessment (HHRA) as a method for analyzing the health threat of nitrate.

Human health risk assessment is an important aspect of environmental and public health management that aims to establish data linkages between human health and the ecosystem(Monosson, 1996). Since long-term consumption of nitrate-contaminated groundwater can result in an elevated risk of certain diseases, the U.S. Environmental Protection Agency (EPA) developed the Nitrate Indicator Health Risk Determination (NIHRD) methodology, which combines oral (drinking intake) and dermal exposure routes to determine the carcinogenic and non-carcinogenic health risk results of nitrate contamination levels in local populations.

In order to investigate the environmental status of groundwater quality in the context of agricultural activities in northern China, the main pollution indicators of the groundwater environment were summarized, and on this basis, the analysis of the sources of pollution impact and health risk assessment were carried out. In this paper, the source of underground drinking water in the main urban area of Zhangjiakou is taken as the research object, the water quality indicators are standardized by using the single-factor evaluation index, the main pollution contributing indicators and the correlation of factors are calculated by using Principal Component Analysis (PCA), and the causes of the changes in the concentration of the main pollutant indicators are discussed in terms of the land use situation, etc., and the level of the impact of the pollution on the health risk of the local residents is calculated in the end.

2. Materials and methods

2.1. Subsection

The study area is located in Zhangjiakou City in the northwestern part of Hebei Province, China, and contains Chongli District and Zhangjiakou main urban area (Bridge-west district and Bridge-east district), which are divided into three different zones according to the source of underground drinking water, and the groundwater monitoring points are the Taobeiying water source zone (TW, E114.92 N 40.89) and the Gushi water source zone (GW, E114.89 N 40.87) in the upstream Chongli District and the Yaozhanbu water source zone (YW, E114.85 N 40.74) in Bridge-west district (Figure 1). The groundwater in this area belongs to the subregion of pore and fissure groundwater resources in the middle and upper reaches of the Yongding River basin, and the groundwater types of the underground rock strata in Chongli are fissure water of mountain metamorphic rocks, fissure water of magmatic rocks of mountains and hills, and near the downstream urban area, pore water of alluvial layers in the intermountain basins, and fissure water of karst mountain fissures and caves, which is very much associated with the distribution of the water types and the ancient crustal activities of the earth's surface topography and the climate of the area is temperate continental monsoon. The regional climate is temperate continental monsoon climate, located in the semi-arid and arid forest-steppe transition zone, with cool and dry temperatures, and the surface elevation decreases from northeast to southwest, which has led to the formation of a certain scale of cities in the southwest flat zone.

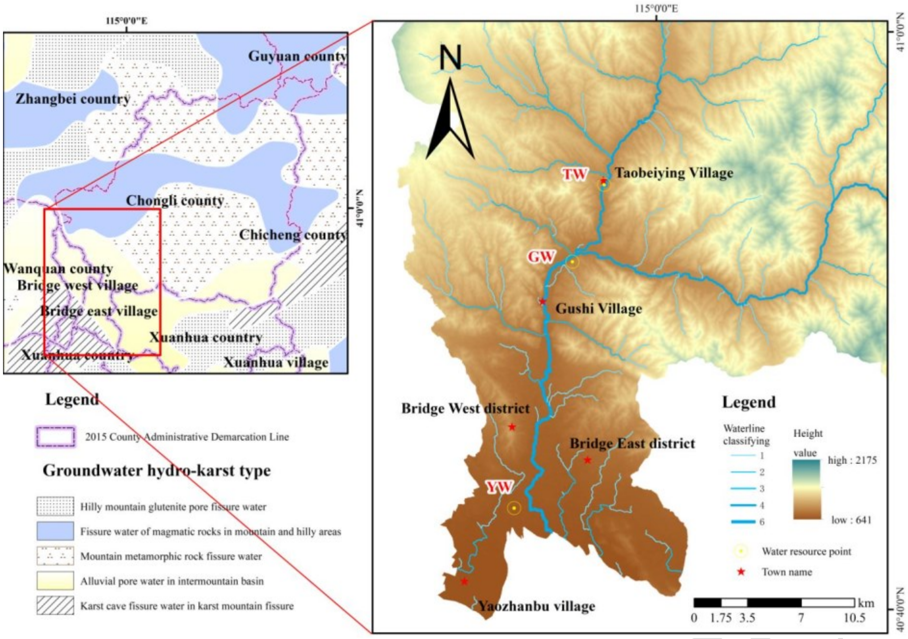


Figure 1. Distribution of elevation and surface river systems and karst types in the study area

2.2. Data sources and research methods

2.2.1. Data sources

Groundwater monitoring wells were collected once a month from January 2021 to November 2023. Each sampling uses a high-density polyethylene bottle and glass bottle cleaned according to the collection requirements to collect 500ml of groundwater, respectively, stored in a 4 ℃ environment, waiting for detection. When collecting water samples, the TDS analyzer is used to directly determine the detection value. Filter with 0.45 μm filter membrane before detection. Metrohm MIC Ion Chromatograph (Switzerland) were used to analyze the concentrations of ammonium and nitrate, chloride, fluoride, sulfate. The detection limits were 0.002 mg L^{-1} and 0.15 mg L^{-1}, 0.15 mg L^{-1}, 0.1 mg L^{-1}, 0.75 mg L^{-1}, respectively. The oxygen consumption was detected by acidic potassium permanganate titration, and the detection limit was 0.05 mg L^{-1}. The total hardness was also detected by titration tube, and the minimum detection concentration was 1.0 mg L^{-1}. Iodide and nitrite nitrogen were detected by spectrophotometry, and the detection limits were 0.001 mg L^{-1}. Sodium, copper, manganese, zinc, aluminum and arsenic were determined by inductively coupled plasma emission spectrometry. The detection limits were 6.36 μ g L^{-1}, 0.08 μg L^{-1}, 0.12 μg L^{-1}, 0.67 μg L^{-1}, 1.15 μg L^{-1} and 0.12 μg L^{-1}, respectively. Radiation alpha and beta were measured by thick sample method and thin sample method, and the detection limits were 0.016 Bq L^{-1} and 0.028 Bq L^{-1}, respectively. The above indexes were self-checked in the laboratory. Blank sample and parallel sample were established, and the standard deviation value was less than 5 %.

China's multi-period land use/land cover data were produced by Esri in conjunction with Impact Observatory and Microsoft's 10-meter-resolution satellite data based on Sentinel-2; atmospheric rainfall, cultivated irrigated area, crop cultivation area, and livestock and poultry production data were obtained from the *2015-2022 Hebei Statistical Yearbook*.

2.2.2. Human health risk assessment

Human health risk assessment is used to quantitatively analyze the relationship between groundwater quality and local human health risk, and to assess the likelihood of damage to human health caused by exposure to chemical substances in a contaminated environment. Because groundwater environments are relatively confined, contaminants relative to the human body are generally considered only through two routes: oral and dermal absorption(Liu et al., 2021). In this study, calculations were performed using a risk model developed by the EPA.

Dose of non-carcinogens ingested through drinking water:

$$\mathrm{CDI} = \frac{\mathrm{C_w \times IR \times EF \times ED}}{\mathrm{BW \times AT}} \tag{1}$$

$$\mathrm{HQ_{Oral}} = \frac{\mathrm{CDI}}{\mathrm{RfD}} \tag{2}$$

In:

CDI——Daily dose for chronic intake of drinking water ((mg kg^{-1})d^{-1});

C_w——Mass concentration of non-carcinogenic substances (mg L^{-1});

IR——Daily human intake of drinking water (L d^{-1});

EF——Exposure frequency (365d a^{-1});

ED——Exposure time;

BW——Average human weight (kg);

AT——Mean time to produce non-carcinogenic effects (d);

$\mathrm{HQ_{Oral}}$——Non-carcinogenic risk index for drinking water intake;

RfD——Reference dose of pollutant (RfD for nitrate is 1.6(mg kg^{-1})d^{-1}).

Dose of non-carcinogens absorbed through the skin:

$$\mathrm{CDD} = \frac{\mathrm{C_w \times K_i \times SA \times EF \times ED \times EV \times ET \times CF}}{\mathrm{BW \times AT}} \tag{3}$$

$$\mathrm{HQ_{Dermal}} = \frac{\mathrm{CDD}}{\mathrm{RfD}} \tag{4}$$

$$\mathrm{HI_{Total}} = \sum_{\mathrm{i-1}}^{\mathrm{n}} (\mathrm{HQ_{Oral}} + \mathrm{HQ_{Dermal}}) \tag{5}$$

In:

CDD——Daily dose for chronic absorption through the skin ((mg kg^{-1})d^{-1});

$\mathrm{K_i}$—— Skin permeability coefficient in water (cm h^{-1});

SA——Average human skin surface area exposed to contaminated environment (cm^{2});

EV——Average bathing frequency, based on 1 bath per day;

ET——Average bathing time;

CF——Volume conversion factor (L (cm^{3})$^{-1}$);

$\mathrm{HQ_{Dermal}}$——Non-carcinogenic risk index from dermal contact;

$\mathrm{HI_{Total}}$——Total non-carcinogenic risk index;

N——Number of pollutants to be evaluated.

Carcinogenic risk through drinking water intake:

$$\mathrm{CR = CDI \times CSF} \tag{6}$$

CR——Indicates cancer risk through oral intake;

CSF——Indicates carcinogenicity slope factor (1×10^{-5}((mg kg^{-1})d^{-1}）$^{-1}$).

In this study, only nitrate was used as a risk factor, and the number of pollutants to be evaluated was $N = 1$. The selection of parameters and the categorization of the target population for evaluation are shown in Table 1.

Table 1. Evaluation parameters of pollution for each target group

parameter	Infant (1 year old)	Children (average age 12 years)	Adult males (average age 30 years)	Adult females (average age 30 years)	reference source
IR	1	1.8	2.5	2.5	(USA.EPA, 1989, Han et al., 2021)
EF	365	365	365	365	(USA.EPA, 1989)
ED	1	12	30	30	(Wu and Sun, 2016)
BW	10	30	74	57	(Han et al., 2021, Institute of Sports Science, 2022)
AT	365	4380	10950	10950	-
RfD	1.6	1.6	1.6	1.6	(USA.EPA, 1989)
K_i	0.001	0.001	0.001	0.001	(Han et al., 2021)
SA	5000	12000	16000	15000	(China, 2019, Han et al., 2021)
EV	1	1	1	1	(Wu and Sun, 2016, China, 2019)
ET	0.5	0.2	0.3	0.5	(Han et al., 2021)
CF	0.001	0.001	0.001	0.001	(Liu et al., 2021, Han et al., 2021)

3. Results

3.1. Analysis of routine water quality indicators

From the data of groundwater source monitoring points in Zhangjiakou from January 2021 to November 2023 (Table 2), it can be seen that the overall concentration level of oxygen consumption in GW, TW, and YW areas is maintained at 0.75±0.28 mg L^{-1}, the concentration level of total hardness (in terms of $CaCO_3$) is 349.29±16.70 mg L^{-1}, the concentration of total dissolved solids (TDS) is maintained at 472.63±74.23 mg L^{-1}, reducing organic matter in GW and TW at a higher level, total hardness is the opposite, in the southern part of the city's groundwater belongs to the low-mineralization water, low salinity; water source monitoring indicators of halide to chloride (Cl^-) as the main body of the overall concentration of 36.84±7.78 mg L^{-1}, and sodium ions (Na^+) to maintain at the same level of concentration; sulfate (SO_4^{2-}) like substances concentration of 73.12±15.19 mg L^{-1}, nitrate (NO_3^-) in the inorganic nitrogen class occupies 97.53%~99.93% of the overall, nitrite (NO_2^-) and ammonia nitrogen (NH_4^+) in the water source concentration level is almost the same, and NO_3^- concentration in TW is significantly higher than the level of other monitoring water sources; metal elements and arsenic elemental content is maintained at the same level, zinc (Zn), aluminum (Al) concentration is higher, respectively, for 0.0046± 0.0072 mg L^{-1} and 0.0030±0.0051 mg L^{-1}, and the average concentrations of copper (Cu), zinc, aluminum, and arsenic (As) elements in groundwater north of the city are higher than those south of the city; the drinking water source radiation measurements are all kept below the guideline values, but with a greater degree of dispersion.GW and TW are involved in a relatively close range, and the data bases and trends of changes in the monitoring are somewhat similar, and they are subjected to anthropogenic activities. Strongly influenced by anthropogenic activities, YW has low concentrations of organic and dissolved substances, high total hardness, and is more deeply influenced by dissolution of natural subsurface rock formations.

Figure 2 shows the correlations between the water quality indicators, and the significance of most of the correlation indicators meets the probability limit of $p \leqslant 0.01$ and 0.05, which is statistically significant. Among them, radiation alpha and radiation beta are highly significant correlation, the correlation coefficient is 0.86, positively promote each other, and at the same time radioactive substances and NO_2^- also have highly significant positive correlation, along with the increase of NO_2^- concentration level, the release of radioactive substances increased; Secondly, there is a highly significant positive correlation between SO_4^{2-} and NO_3^-, the correlation coefficient is 0.76, the two have a very close correlation; NO_3^- and manganese (Mn), total hardness and Cu, but the correlations were low, with correlation coefficients less than 0.4.

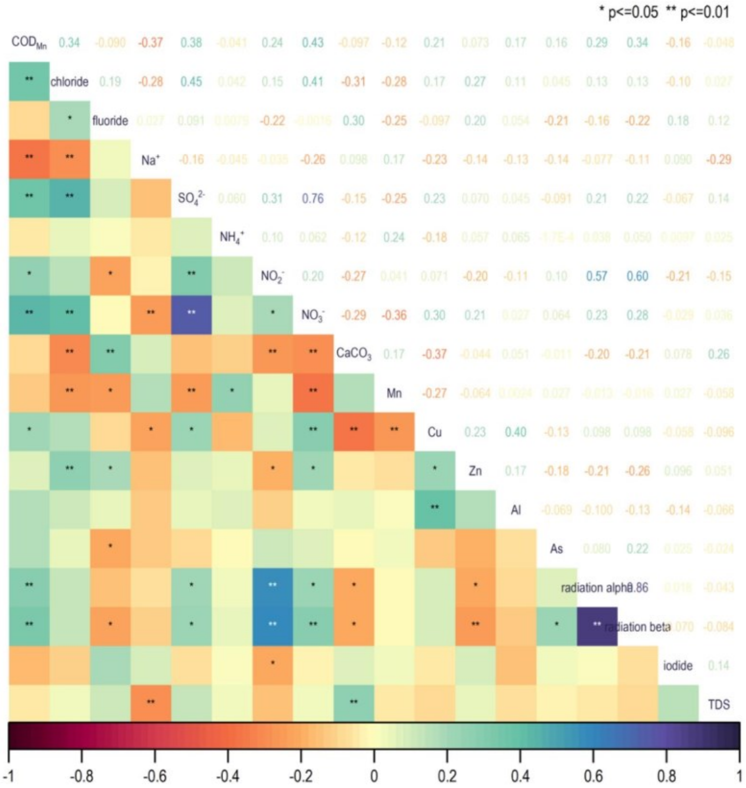


Figure 2. Heat map of significant correlations of water chemistry indicator data

Table 2. Statistics on groundwater quality indicators in the monitoring area

norm	items	GW	TW	YW	the total
COD_{Mn}	Mean/SD	0.83±0.20	0.85±0.17	0.56±0.33	0.75±0.28
$CaCO_3$	Mean/SD	345.09±16.91	347.94±14.98	354.83±16.61	349.29±16.70
TDS	Mean/SD	477.57±83.12	476.51±67.44	463.8±70.32	472.63±74.23
Cl^-	Mean/SD	41.01±5.75	38.22±8.83	31.30±4.56	36.84±7.78
F^-	Mean/SD	0.71±0.14	0.67±0.11	0.61±0.08	0.67±0.12
I^-	Mean/SD	0.003±0.004	0.004±0.005	0.005±0.005	0.004±0.005
Na^+	Mean/SD	34.41±7.86	33.86±7.21	43.57±9.03	37.28±9.21
SO_4^{2-}	Mean/SD	76.55±13.19	80.16±17.85	62.67±5.40	73.12±15.19
NH_4^+	Mean/SD	0.019±0.027	0.019±0.030	0.019±0.028	0.019±0.029
NO_2^-	Mean/SD	0.0020±0.0031	0.0020±0.0031	0.0020±0.0031	0.0020±0.0031
NO_3^-	Mean/SD	10.97±2.84	12.13±2.55	7.55±1.27	10.22±3.03
Mn	Mean/SD	0.0006±0.0009	0.0008±0.0010	0.0024±0.0020	0.0012±0.0016
Cu	Mean/SD	0.0014±0.0007	0.0013±0.0005	0.0009±0.0004	0.0012±0.0006
Zn	Mean/SD	0.0053±0.0073	0.0063±0.0081	0.0022±0.0050	0.0046±0.0072
Al	Mean/SD	0.0045±0.0068	0.0032±0.0047	0.0014±0.0017	0.0030±0.0051
As	Mean/SD	0.0007±0.0006	0.0010±0.0005	0.0009/0.0006	0.0009±0.0006
radiation alpha	Mean/SD	0.073±0.110	0.058±0.082	0.048±0.065	0.060±0.089
radiation beta	Mean/SD	0.076±0.090	0.069±0.062	0.054±0.062	0.067±0.073

3.2. Analysis of major groundwater contamination indicators

Since different water quality indicators have different concentration limits that cause harm to human beings, each country has limited different indicator limits in combination with multiple conditions and uses. According to the drinking function of groundwater in the study area, the Class III standard in China's *Groundwater Quality Standard (GB/T 14848-2017)* and the *Hygienic Standard for Drinking Water for Daily Life (GB 5749-2022)* were adopted as the unification conditions for the indicators, respectively, so as to eliminate the differences in the concentrations of different quantities, and the processed data were brought into the box-and-line diagrams for analysis.

Harmonized formulae refer to single-factor pollution indices for water quality evaluation P_i:

$$P_i = C_i / S_i \tag{7}$$

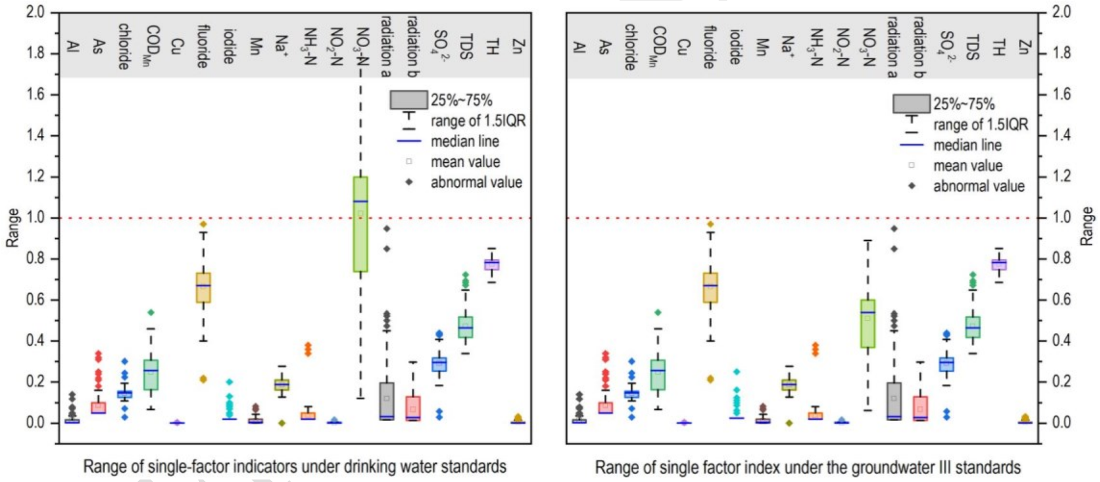
In: C_i is the measured concentration of the ith water quality indicator (mg L^{-1}); S_i is the evaluation standard of the ith water quality indicator (mg L^{-1}).

As can be seen from **Error! Reference source not found.**, the indicators under the Class III standard in the *Groundwater Quality Standard (GB/T 14848-2017)* are all less than 1, while only nitrate appears to be greater than 1 under the Health Standard for *Hygienic Standard for Drinking Water for Daily Life (GB 5749-2022)* as the standard, which indicates that only NO_3^- appears to be more than the drinking water hygiene standard under the two standards, and the other indicators are all under the concentration range specified by the target water function. This indicates that under the two standards, only NO_3^- exceeds the drinking water health standard, while the other indicators are in the concentration range specified by the target water use function, and NO_3^- has appeared in the groundwater of Zhangjiakou City, which affects the normal use of drinking water. Besides, nitrate has the widest interquartile range and no outliers, so the results are good.

Using SPSS 25 for PCA calculation, the KMO value of the 18 indicators involved in the calculation was 0.6, Bartlett's spherical test $P < 0.001$, and the correlation matrix conformed to the normal distribution, which fulfilled the pre-calculation requirements. The eigenvalue mapping and ellipse confidence were shown in **Error! Reference source not found.**(a). The top two main influencing factors from groundwater pollution were 20.5% and 14.0% contribution rate respectively, in which NO_3^- had the highest correlation with Factor 1 and was positively correlated; SO_4^{2-} and NO_3^- indicator eigenvalues tended to converge, and the enhancement of Factor 1 sources would promote the elevation of SO_4^{2-}, NO_3^-, COD_{Mn} , and Cl^- concentrations; Zn showed the main positive correlation in Factor 2, followed by radioactive substances showed negative correlation, in which the downscaling tendency of NO_2^- almost overlapped with radioactive substances with high correlation. The data downscaled elliptic confidence intervals of GW and TW overlap to a high degree, and the TW confidence interval is contained within the GW interval. There are some similarities in groundwater chemistry types and pollution sources between the two places, and the downscaled projection of YW indicators is more concentrated, forming two different systems with TW and GW groundwater environments.

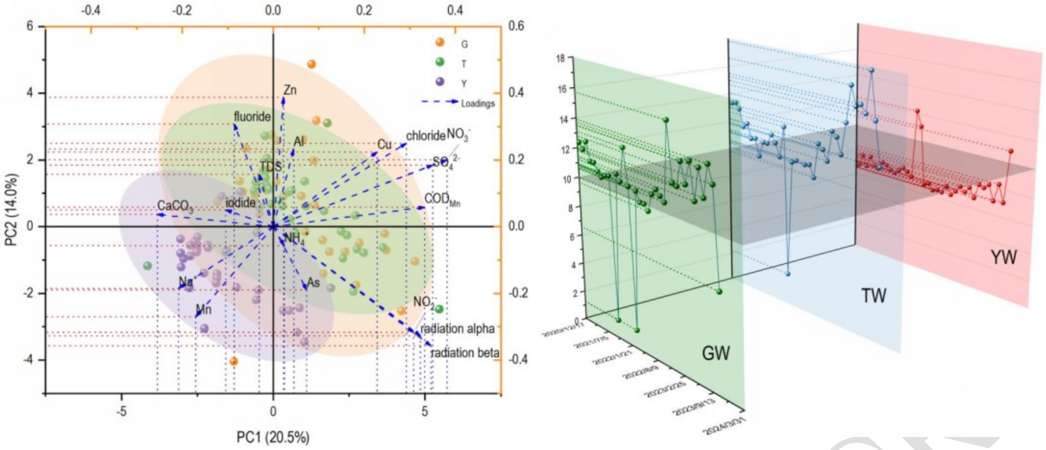
Principal components extracted from the two-dimensional data projection formed in the ellipse confidence, choose the Kaiser normalized maximum variance method for the rotation of the component matrix, and converge after nine iterations, to get the rotated component matrix in **Error! Reference source not found.**. The maximum correlation index of the highest contributing principal component, factor 1, was nitrate with a correlation coefficient of 0.808, followed by positive correlations of 0.795 for SO_4^{2-} and 0.738 for Cl^-, and an increase in the source of factor 1 leads to an increase in the concentration of salts, and the preliminary type of the factor 1 source was residential sewage or inputs from inorganic fertilizers in agriculture; Indicators closely related to the source of factor 2 are radioactive substances, which show positive correlation, NO_2^- shows a correlation of 0.72 in factor 2, which comes from radionuclide decay in the natural environment; Al and Cu are the main correlation indicators of factor 3; the top three component factors occupy 39.301% of the total variance after rotation, and based on the eigenvalues, the top seven screening factors selected greater than 1, the occupied 69.843% of the total variance.

Comprehensive single-factor indicator range distribution and PCA factor analysis results show that the increase in nitrate concentration is the main cause of pollution of underground drinking water sources in Zhangjiakou City, and the correlation indicators of SO_4^{2-} and Cl^- among the maximum pollution factors did not appear to exceed the limiting standards in the actual measurement. Combined with the monthly trend of NO_3^- concentration from 2021 to 2023 (**Error! Reference source not found.**(b)), the overall fluctuating upward trend of NO_3^- concentration in GW and TW, except for some months the NO_3^- concentration in drinking water sources north of the city exceeded the limit value of drinking water health standards. The degree of concentration variability was higher in TW than in GW, and the NO_3^- concentration in YW remained stable between 6 mg L^{-1} and 8 mg L^{-1} for most of the time, with the lowest level of contamination. Overall, TW showed obvious water quality problems, and the exceedance of NO_3^- concentration was the main manifestation of pollution problems in this shallow groundwater, and there was a trend of superimposed increase in NO_3^- concentration in the groundwater with the increase of time.



(a) **(b)**

Figure 3. Box plots for each indicator based on the results of single factor calculations for (a) drinking water standards and (b) groundwater class III standards



(a) **(b)**

Figure 4. (a) Indicator factor fits and confidence intervals for principal component analysis and (b) changes in monthly nitrate indicator concentrations in water sources

Table 3. Rotated component matrix

norm	Faction 1	Faction 2	Faction 3	Faction 4	Faction 5	Faction 6	Faction 7
F^-	0.282	-0.226	-0.043	0.493	-0.485	-0.091	0.138
Na^+	-0.341	-0.004	-0.363	-0.204	-0.605	-0.007	-0.085
SO_4^{2-}	0.795	0.244	0.022	0.080	-0.110	0.001	-0.073
NH_4^+	0.142	0.013	-0.043	-0.049	-0.017	0.859	0.052
NO_2^-	0.187	0.720	-0.086	-0.200	-0.008	0.131	-0.228
NO_3^-	0.808	0.183	0.062	-0.114	0.090	-0.056	0.059
$CaCO_3$	-0.305	-0.117	-0.053	0.815	-0.109	-0.035	-0.118
Mn	-0.502	0.097	0.028	0.046	0.036	0.632	-0.073
Cu	0.204	0.090	0.714	-0.363	-0.016	-0.313	0.131
Zn	0.329	-0.379	0.394	-0.059	-0.118	0.183	0.302
Al	-0.014	-0.097	0.800	0.085	-0.065	0.083	-0.233
As	-0.035	0.075	-0.250	-0.050	0.733	-0.022	-0.060
radiation alpha	0.102	0.917	0.026	-0.035	0.020	-0.001	0.124

radiation beta	0.124	0.906	-0.026	-0.074	0.151	-0.009	0.018
I^-	-0.100	-0.007	-0.102	0.089	-0.065	-0.002	0.856
TDS	0.131	-0.066	0.002	0.618	0.258	0.033	0.344
Cl^-	0.738	-0.013	0.088	-0.072	0.063	0.042	-0.059
COD_{Mn}	0.443	0.314	0.301	0.100	0.342	-0.051	-0.254

3.3. Analysis of the causes of changes in nitrate concentrations

Most studies have shown that synthetic fertilizers, livestock manure, domestic and industrial wastewater, atmospheric deposition, natural organic matter of soil, septic tanks and landfills are the main sources of nitrate pollution(McLay et al., 2001, Gutiérrez et al., 2018, Gan, 2023). Zhangjiakou, as a typical city focusing on primary industry economy, the study area has frequent agricultural farming activities, the water surface is covered with a large area of facility farmland, and the utilization of land is crucial to the impact of groundwater environmental pollution. The common dissolved nonpoint source pollution in agricultural watersheds includes two major sources, anthropogenic and natural, and the lost part of the natural source is not a pollutant in the strict sense, but the tracing of the pollution source inevitably needs to determine the contribution of the natural source(Nie, 2016).

The anthropogenic sources of pollution in the study area include fertilizer and drug application losses from crops, leakage of manure wastewater from livestock and poultry farming, and rural and urban domestic sewage discharges, while the natural sources include atmospheric precipitation, natural organic matter of the soil, inputs, runoffs, and outputs of terrestrial sources such as subsurface karst and other substances in the groundwater system, as well as physiological survival of plants, animals, and microorganisms. In the following, we will analyze the reasons affecting the level of nitrate concentration in groundwater from the aspects of land use, precipitation changes and agricultural activities.

3.3.1. Impact of land use status and migration on nitrate pollution

According to Figure 5, it can be seen that the upper part of the main urban area has grassland as the main land use type, and the cultivated area is distributed in the flat beaches along both sides of the river, and the urban settlements are scattered, sparsely populated, and have not formed a large-scale city; Bridge-west district and Bridge-east district have built-up areas and grassland as the main land use types, followed by cultivated land distributed in the lower part of the city. Forest land is small and concentrated in the northwest corner away from urban agglomerations.TW, GW and YW land cover types are very different.

The buffer zones of 300 m, 500 m, 800 m, 1000 m, and 1200 m distance were divided respectively with the monitoring point as the center, and the land use transfer matrix of the buffer zones in 2021-2022-2023 was established (Figure 5).The land types of the buffer zones from 300 m to 1000 m in TW were built-up area and grassland, and with the increase of buffer area, the percentage of built-up area was gradually decreasing and grassland becomes the main land use type in the area with simple land use transfer. Grassland accounts for the largest proportion of land use in the vicinity of GW, and the proportion of built-up area and cropland area gradually increases with the increase of buffer distance, and there is a mutual transfer of the utilization of grassland and cropland, and on the whole, the area of cropland shows a significant increase with the change of time, and the use of grassland for clearing the land is the main source of its contribution. the area of built-up area of YW occupies an absolute dominant position in the buffer zones of different distances , the share of watershed is decreasing in the growing buffer area, the growth and utilization matrix of grassland type changes significantly below 800 m distance, a significant urban expansion occurs in 2022, erosion of grassland area, between 800 m, 1000 m, and 1200 m distance buffer ranges, cropland becomes a secondary land use type other than built-up area, and the land use transfer situation is complex.

The urbanization of the study area deepens year by year, and the town land starts to spread to the surrounding, the degradation of the grassland is affected by the cultivated land clearing and urban expansion, the water collection area of the study is less affected by the mountain forest cover, the forest land has been in a low development and high protection use state, and the agricultural cultivation area is still increasing. The TW and GW collection areas upstream of the urban area are mainly influenced by grassland, with simple land use composition, clear and simple matrix changes, and low and flat terrain; the main land use type of the downstream YW collection area is construction area, which is little influenced by land cover with high soil permeability coefficient such as grassland cropland, and the terrain is higher and subject to hydraulic impacts from the upper reaches and hills on the two sides. Changes in the proportion of land use types are closely related to local agricultural and economic development, climatic conditions, urban planning and other environmental policies. Combined with the contamination level of nitrate in different areas, the low concentration level of nitrate indicator in YW groundwater may be related to the high degree of land hardening in the construction area, the small permeability coefficient of the soil, and the slow rate of contamination input from human activities, and in the YW and TW areas, which are dominated by grass, the nitrate level of the groundwater is high, and there is a prolonged period of exceeding the standard, and the high-frequency contamination from the nearby areas of human agricultural activities aggregation and pollution transformation products from the natural environment seeped into the groundwater through the loose soil. According to Xu et al.'s study on the water quality of surface rivers in Zhangjiakou urban area(Xu et al., 2023), the overall concentration of total nitrogen in surface water averaged 5.87 mg L^-, and the nitrogen pollution of groundwater was rather more serious than that of the surface, and the inputs of nitrate from surface water to groundwater were almost small, and the pollution mainly entered the groundwater system through soil.

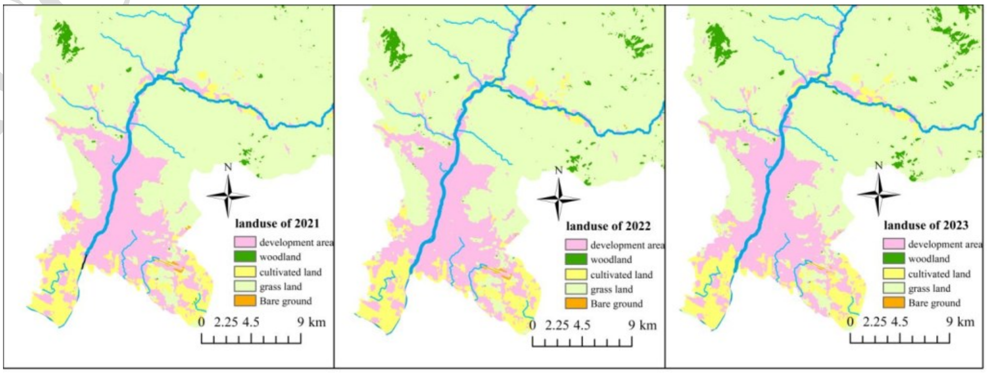


Figure 5. Land use types in the study area, 2021, 2022, 2023

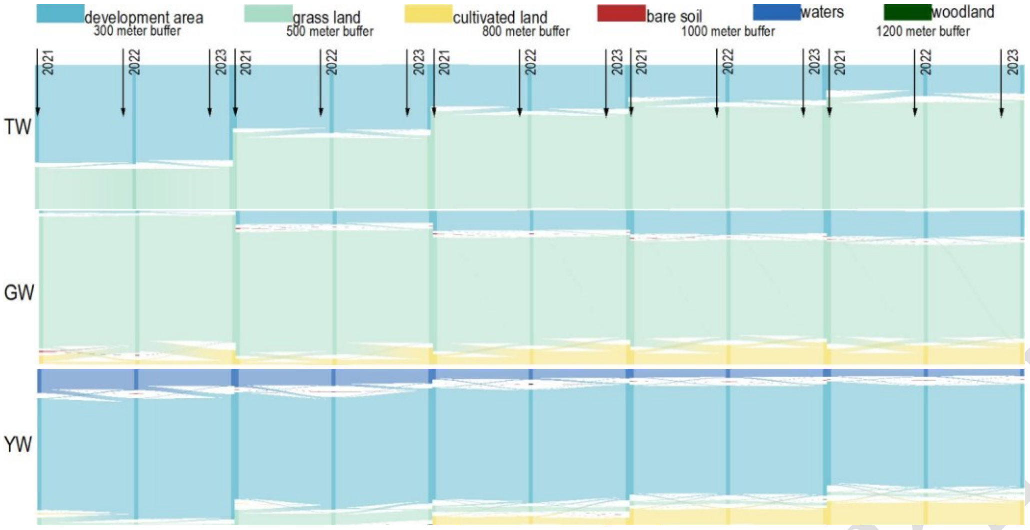


Figure 6. Land use migration in the last three years under 300m, 500m, 800m, 1000m, 1200m buffer diameters for TW, GW, YW

3.3.2. Effect of precipitation on nitrate pollution

Soil infiltration and surface water replenishment and discharge are closely related to atmospheric precipitation, which is the main source of replenishment of local groundwater resources.The groundwater level in the study area is controlled by precipitation, and the water level drops to the lowest value in December, and the highest value of the water level of the whole year can generally be reached in August to September(Chen, 2020). The statistical yearbook data shows that the average annual precipitation in 2022 and 2023 is 378.2 mm, which is in the dry year and mostly concentrated in June to September in the form of showers, with poor groundwater recharge conditions. The study area is the demarcation zone between semi-arid and semi-humid, and the demarcation zone between forest vegetation and grassland vegetation.

The hydrodynamic forces generated by atmospheric rainfall drive the transport of soil nitrogen into the groundwater environment through infiltration and runoff. Many studies have shown that in forested watersheds with low precipitation, the soil retains most of the rainwater, resulting in nitrification reactions that increase the NO_3^- content of the soil water, which ultimately enters the groundwater body through leaching and infiltration(Phillips and Koch, 2002, Kumar et al., 2004, Pardo et al., 2004). For vegetable agriculture planting areas, sustained heavy rainfall will elute the remaining NH_4^+ in the air-packed zone, and nitrification produces more NO_3^- into the shallow groundwater, and isotope traceability shows that the proportion of NO_3^- in the shallow groundwater during periods of heavy precipitation from manure increases, and the proportion of NO_3^- from soil organic nitrogen decreases(Chen et al., 2023). After linear fitting, precipitation and groundwater nitrate concentration showed a poor negative linear relationship, which may be due to the sudden precipitation situation to increase the amount of surface water, and the different sources of the combined effect of supplemental dilution strengthened, accelerated the rate of circulation of underground and surface water bodies, and improved the environmental conditions of groundwater. Moreover, according to the field research, surface farming in the study area is dominated by facility farmland, and the agricultural greenhouses and mulch erected for cash crops affect the infiltration of precipitation into the soil and soil water migration.

3.3.3. Impact of agricultural activities on nitrate pollution

Based on the statistical yearbook data from 2015 to 2022 that the area under crop cultivation rises slowly after 2021, which is consistent with the annual change in the area of land use type of arable land, and cereals and vegetables are the main types of cultivated plants; the amount of agricultural fertilizers applied decreases and stays at 129,000 tons after reaching a peak in 2018 and 2019, and the amount of fertilizers per unit of arable land decreases from 2021 to 2022; the local area is mainly dominated by cattle as the large livestock farming, livestock farming volume is in a trough between 2017 and 2020, and has rebounded in the past two years. Influenced by the type of surface cover, agricultural activities are still one of the main influencing factors for the change of pollutant concentration in the water collection area. The microbial life activities under different precipitation seasons, types of cultivated crops, livestock and poultry activities, selection and regulation of fertilizer application, as well as different soil temperatures, humidity, and acidity and alkalinity differed. According to Duan's study(Duan et al., 2023), the main sources of nitrate pollution in surface water of the lower Wei River and groundwater in the river floodplain, alluvial plain and loess plateau areas were livestock and poultry manure and domestic sewage (32.6 %), animal manure and domestic sewage (43.7 %), animal manure and domestic sewage (59.1 %), and atmospheric deposition (55.5

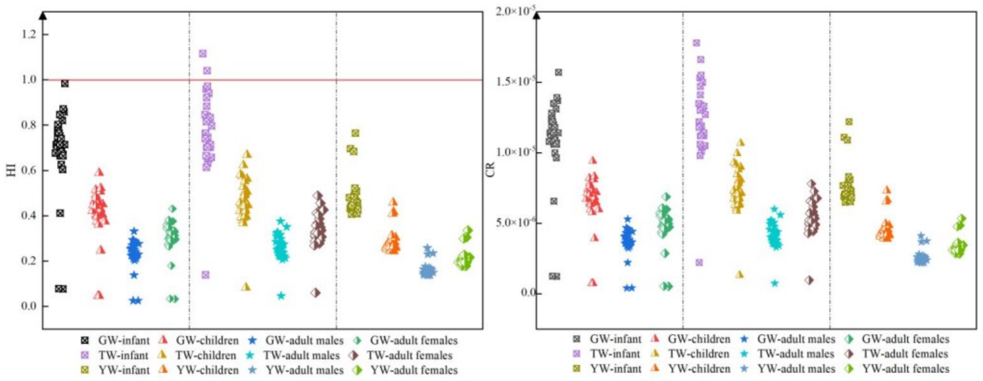
%) respectively. Nitrate from agricultural activities is transported to surface or groundwater systems through, for example, soil leaching. Identification of the source of nitrate in soil filtrate under conditions that limit microbial transformations revealed that 18% to 41% of nitrate originated from rainfall, 38% to 57% from mineralization of soil organic matter in the rhizosphere of non-leguminous plants, and 18% to 40% of nitrate originated from mineralization of soil organic matter in the rhizosphere of leguminous plants(Oelmann et al., 2007). Using water chemistry methods and environmental isotope techniques, the analysis of shallow groundwater of different land use types in Wanzhou District, Chongqing shows that nitrate in shallow groundwater of arable land mainly comes from chemical fertilizers (36.3%), sewage manure (35.4%) and soil organic nitrogen (24.7%), and that the sources of nitrate in shallow groundwater of the study area are dominated by chemical fertilizers and sewage manure as a whole(Fan et al., 2023). In general, the sources of nitrate pollution in the context of agricultural activities are closely related to the application of agricultural fertilizers, the treatment of livestock and poultry manure, the discharge of rural sewage, and the organic mineralization of soil.

3.4. Human health risk assessment

According to the EPA's health risk assessment standards, when $\mathrm{HI_{Total}} < 1$, the non-carcinogenic health risk of pollutants to human beings is acceptable, the pollutant does not cause significant damage to humans; when $\mathrm{HI_{Total}} > 1$, it indicates that the non-carcinogenic risk caused by the pollutant has exceeded the acceptable level, and that the non-carcinogenic health risk increases with the increase of $\mathrm{HI_{Total}}$, and there is a increasing trend(Feng et al., 2020). According to the calculation results in 0(a), it can be seen that the non-carcinogenic health risk of nitrate contamination of groundwater as a source of drinking water is not high. In the vicinity of GW and YW, monthly samples of infants, children, adult males, and adult females meet the standard; only in TW, there is a non-carcinogenic health risk of nitrate contamination for infants that exceeds the acceptable level, which is 1.04 (May) and 1.12 (September) in 2023, respectively. The non-carcinogenic health risk due to nitrate groundwater contamination in GW and TW is low for children, adult males, and adult females, but cannot be ignored for newborns, and there is a high likelihood that this non-carcinogenic risk will continue to increase based on the trend of contaminant growth from year to year. And according to the conclusion of Jane et al (Lin et al., 2023), it is known that low and medium concentrations of nitrates in drinking water may increase the risk of preterm birth, some specific congenital malformations.

The carcinogenic risk CR value is in the range of $1 \times 10^{-6} \sim 1 \times 10^{-4}$, the risk of occurrence is at an acceptable level; if $\mathrm{CR} > 1 \times 10^{-4}$, the carcinogenic risk exceeds the maximum acceptable level (Jiang et al., 2017). According to Figure 7(b), the carcinogenic risk values of the study subjects were in the range of acceptable levels, with zero exceedance and very low risk values.

Although exceedances of the nitrate standard occurred in the GW and TW, the pollution level was low, the health risk evaluation value for the local residents was low, and the majority of the residents were given a non-carcinogenic risk and a low level of carcinogenic risk, but for newborn babies, the low concentration of nitrate can still cause physiological adverse effects for this group. Combining the land use and temporal node characteristics of the high-risk samples, TW is located in the lower reaches of the Qingshui River Basin in Chongli District, where the land cover is dominated by grasslands, and more clustered villages are distributed along the arable land and around the river, and after a field visit, it was found that the ground surface is covered with a large area of agricultural land dominated by large greenhouse cash crops, such as maize and colorful peppers, and that the roots of non-soybean crops play a stronger role in mineralization of nitrogen in the soil, the Rural domestic sewage, greenhouse plastic film, agricultural inorganic synthetic wastes, and livestock manure play a co-influence on the growth of local groundwater nitrate concentrations. The months when the risk value exceeded the standard coincided with the beginning and the end of the cultivation period. Frequent agricultural activities and the wet and warm climate increased the nitrogen load in the soil and accelerated the rate of recycling and seepage of nitrogen accumulated in the soil in the previous period, which led to a sudden increase in the nitrate concentration in the groundwater.



(a) (b)

Figure 7. (a) Evaluation results of non-carcinogenic health risks and (b) carcinogenic risks for different groups of local residents

4. Discussion

Contaminants generally enter the groundwater system through the soil. It is inferred that nitrate contamination is more influenced by rural human activities, livestock farming, and cultivation from grasslands and nearby than from municipal domestic sewage and industrial water from more urbanized built-up areas, and that the state of the soil will control nitrate inputs. Nitrate has relatively low pollution concentrations, and is characterized by non-overlap in time with traditionally indicated sources such as: flood season and periods of high agricultural activity. The reason for this may be due to the retention properties of the soil, which can trap pollutants from the surface, e.g. the transformation of some organic nitrogen species in the soil requires the involvement of microorganisms, however, the longer winters keep microbial activity depressed for a long period of time. According to Llovet et al.(Margalef Marti et al., 2021)' s study of soil extracts after the application of pig slurry, it is known that soil mineralization and migration of contaminants by percolation to groundwater requires time for migration.

Combined with the results of the HHRA, the risk of disease from underground drinking water is higher for people living in non-urban areas. Under the current known conditions, the downstream drinking water in the main urban area has a pre-treatment process, but the nitrate removal efficiency does not reach the desired level, which is due to the adjustment of the national limit values for drinking water and the time difference between the upgrading of the process in the water plant; the upstream water source point pollution problem is more serious, and the groundwater as a source of drinking water directly into the villagers' homes, there is no centralized treatment, and the use of groundwater in the form of villages as a unit, it is It is difficult to manage it as a whole. The study area suffers from unsupported urban water supply, lack of rural water supply facilities, and unbalanced development of regional water supply. Rural areas should receive more attention as a vulnerable area in terms of resource tilting and water pollution damage, and it is also a key part of the problem for the region to build a sustainable city with a healthy balance of clean water sources and water resource control.

5. Conclusions

The groundwater in TW and GW is more deeply affected by human activities than in YW, forming Ca-HCO_3 type high salinity and low hardness water quality, and there is a significant correlation between some of the water quality indexes; only the nitrate indexes exceeded the drinking water functional limit in TW and GW, which is also the main pollution problem faced by the groundwater of the whole region, and the nitrate concentration of the groundwater had a tendency to increase with the time scale. The cause of the change in nitrate concentration from the land use aspect can be considered as the land use type with better soil permeability, low hardening of road surface and frequent human agricultural activities such as grassland and nearby human rural activities have a higher impact on the pollution compared to the urban built-up areas. Moreover, pollutants mainly enter the groundwater system through the soil, and there is a certain delay in the outbreak of pollution concentration, and precipitation will dilute and purify the quality of groundwater. In the face of the emergence of nitrate contamination of underground drinking water sources, only newborns in the vicinity of TW will be threatened by the non-carcinogenic risk of nitrate, but due to the existence of an increasing trend of nitrate concentration in the upstream water sources of the urban area, the non-carcinogenic health risk will correspondingly appear to be synchronously elevated.

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