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Hydrochemical characteristics and health risk assessment of groundwater in Wudalianchi County

Youtao Xin[1,2], Jiajia Xu[3]*, Zhongkai Liang[1,2]*, and Haonan Song[1,2]

[1]Environmental Geological Survey Office, Harbin Natural Resources Comprehensive Survey Center, China Geological Survey, Harbin, Heilongjiang, China

[2]Observation and Research Station of Earth Critical Zone in Black Soil, Ministry of Natural Resources, Harbin, Heilongjiang, China

[3]Analytical Laboratory, Heilongjiang Institute of Ecological Geological Survey, Harbin, Heilongjiang, China

Abstract

Groundwater quality in volcanic regions is critical for public health and ecological stability, yet systematic assessments integrating hydrochemical evolution and health risks remain limited. A comprehensive investigation was conducted to elucidate the hydrochemical signatures, governing mechanisms and potability of groundwater in Wudalianchi County. In July 2023, 34 monitoring wells were sampled, and physicochemical parameters—including pH, total dissolved solids, and major cations and anions—were quantified. Multivariate statistics, correlation matrices, and geochemical diagrams were integrated to explore hydrochemical evolution, while the Entropy-weighted Water Quality Index and the United States Environmental Protection Agency's non-carcinogenic risk models were adopted to evaluate water quality and health risks. The groundwater had a pH of 5.87–8.10 (mean = 7.07) and total dissolved solids of 27.75–515.40 mg/L, with dominant hydrochemical facies of HCO_3–Ca and HCO_3–Ca·Na. The average Entropy-weighted Water Quality Index was 44.01 (range = 5.87–197.37), and 35.29% of samples exceeded the nitrate limit. Hazard quotient values for children ranged from 0.03 to 4.36 (mean 0.90), with 29.41% exceeding the threshold; adult hazard quotient values ranged from 0.02 to 3.48 (mean = 0.72), and 23.53% failed to meet the safety standard. Hydrochemical compositions were mainly controlled by lithogenic weathering. Nitrate was the primary pollutant. While most samples were suitable for drinking, groundwater in western urban and industrial areas posed obvious non-carcinogenic risks, especially to children, due to agricultural runoff and domestic sewage discharge. Targeted protection measures are urgently required for these human-disturbed regions.

Keywords: Groundwater; Hydrochemistry; Entropy-weighted Water Quality Index; Health Risk Assessment; Wudalianchi County

***Corresponding authors:**
Jiajia Xu
(312818756@qq.com);
Zhongkai Liang
(lzk_cindy@126.com)

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1. Introduction

Groundwater resources represent an indispensable portion of the global freshwater budget, playing an irreplaceable role in sustaining both ecosystem integrity and hydrological equilibrium.[1-3] The spatial and temporal distribution of dissolved constituents within aquifers reflects a complex interplay between indigenous geochemical reactions and external anthropogenic perturbations, thereby functioning as diagnostic tracers for groundwater system evolution. Meanwhile, because potable aquifers serve as primary drinking water sources for numerous communities, the chemical integrity of such resources directly governs public health outcomes through chronic ingestion exposure.[4-6] Volcanic terrains situated within cold-temperate continental monsoon climatic belts—exemplified by the Wudalianchi volcanic field in northeastern China—present particularly sophisticated hydrogeochemical behaviors. In these environments, the superimposition of volcanic lithology weathering and surface human activities induces marked modifications in ionic assemblages and pollutant loads, rendering systematic quality appraisal and risk characterization essential prerequisites for sustainable watershed management.[7,8]

Despite the ecological and socioeconomic significance of these aquifers, prior investigations have largely concentrated on isolated hydrochemical indicators or single-process interpretations, lacking the systematic integration of geochemical genesis, spatial distribution patterns, and population-scale health risk evaluation. Specifically, several unresolved questions persist regarding the unique volcanic host–rock environment:

(i) What mechanisms dominate the chemical evolution of groundwater in this region?
(ii) To what degree do anthropogenic pollutants—particularly nitrate—compromise aquifer quality, and what are the consequent health implications for sensitive populations such as children?

These knowledge deficiencies have impeded effective groundwater governance and public health protection.[3,9-11]

Recent investigations have demonstrated that volcanic aquifers worldwide are commonly influenced by a combination of silicate and carbonate weathering, ion exchange, hydrological mixing, and land-use–derived inputs.[12] For instance, groundwater chemistry in the Yogyakarta–Sleman volcanic basin exhibits distinct characteristics between unconfined and confined units, governed primarily by silicate weathering and cation exchange.[13] In the Axum volcanic terrain of Northern Ethiopia, dissolution of calcite, dolomite, gypsum, fluorite, and halite—coupled with anthropogenic interference—has been shown to regulate groundwater potability. Within the Meru volcanic complex, fluorine mobility is strongly coupled to parental volcanic materials and soil–rock interactions, indicating that volcanic substrates can also constitute significant geogenic contaminant sources.[14] Furthermore, recharge and mixing dynamics in volcanic aquifers have been documented to vary substantially with precipitation regimes and topographic gradients.[15-17]

Within China, previous Wudalianchi studies have predominantly focused on isotopic tracers, mineral spring characteristics, or localized geochemical attributes, whereas the systematic synthesis of hydrochemical genesis, spatial water quality appraisal, and human health risk quantification remains limited.[11,18-21] Therefore, to the best of our knowledge, the present investigation represents one of the earliest efforts to comprehensively integrate multivariate hydrochemical analysis, entropy-weighted water quality assessment, and health risk evaluation within the cold-temperate volcanic groundwater system of Wudalianchi County. This work not only clarifies the dominant hydrogeochemical processes but also contextualizes the findings against global volcanic-region studies, thereby enhancing the interpretation of its novelty and broader scientific relevance.

This study aims to comprehensively characterize the hydrochemical composition, spatial variability, and formation mechanisms of groundwater in Wudalianchi, while quantifying potential non-carcinogenic health hazards. A multidisciplinary integrated methodology was adopted, encompassing multivariate statistical analysis, Durov diagrams[22], Gibbs diagrams[23], Entropy-weighted Water Quality Index (EWQI)[24], and the United States Environmental Protection Agency (USEPA)'s health risk assessment model.[25]

Comparable integrated approaches have been successfully implemented to evaluate hydrocarbon contamination and associated health hazards.[26] By integrating hydrogeology, environmental chemistry, and public health science, this study aims to fill the gap in systematic hydrochemical and health risk research within volcanic-rock regions. The anticipated outcomes will furnish scientific support for local groundwater resource management, pollution mitigation, and drinking water safety assurance, while offering transferable insights for analogous volcanic settings globally.

The principal novelty of this investigation resides in linking volcanic-rock hydrogeochemistry with spatial water quality evaluation and health risk assessment at the county scale, thereby delivering a more integrated understanding than studies constrained to single processes, individual pollutants, or isolated mechanisms.

2. Sample collection and research methods

2.1. Study area overview

Wudalianchi County is situated in northern Heilongjiang Province, with geographic coordinates extending from 125°42'–127°37'E longitude and 48°16'–48°45' N latitude.

It lies at the transition zone between the Xiao Hinggan Mountains and the Songnen Plain, with topography descending from northeast to southwest. The territory hosts the Wudalianchi volcanic cluster, comprising 14 volcanoes of varying ages and five bead-like barrier lakes, featuring well-developed volcanic landforms. The region experiences a cold-temperate continental monsoon climate, marked by prolonged cold winters and brief warm humid summers, with mean annual precipitation approximating 450–550 mm. Local economic development depends primarily on agriculture, forestry, and tourism, while groundwater constitutes the principal water supply for domestic consumption and agricultural irrigation.

2.2. Sample collection and testing

A total of 34 groundwater sampling and monitoring stations were established across the study domain. Sampling was conducted centrally in July 2023, and the specific spatial distribution of each station is illustrated in Figure 1. The entire water sample collection procedure was conducted in strict accordance with technical specifications outlined in the "Technical Specifications for Groundwater Environmental Monitoring (HJ 164-2020)".

Specialized groundwater sampling apparatus was employed to collect water at wellheads, avoiding secondary contamination throughout the procedure. Sealed samples were transported to the laboratory for analysis, and the following parameters were determined: cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}), anions (HCO_3^-, SO_4^{2-}, Cl^-, F^-, and NO_3^-), and additional key evaluation indicators (total hardness [TH]) and total dissolved solids [TDS]). Detection and analytical methods for all parameters were strictly implemented according to provisions of the "Standard Examination Methods for Drinking Water (GB/T 5750-2023)": Ca^{2+} and Mg^{2+} were quantified by atomic absorption spectrometry (AAS); K+, Na+, and various anions were detected by ion chromatography (ICS-2100); HCO_3^- was analyzed by acid–base titration; total hardness was determined by ethylenediaminetetraacetic acid titration; and chemical oxygen demand was detected by acidic potassium permanganate oxidation.

2.3. Research methods

2.3.1. Hydrochemical data analysis methods

This study adopted multiple data analysis techniques. Firstly, SPSS Statistics version 26 (IBM, USA) was utilized to compute mathematical and statistical parameters for groundwater detection data, deriving statistical metrics including maximum, minimum, mean, standard deviation, and coefficient of variation for each indicator to characterize central tendency and dispersion.[27-30] Secondly, correlation analysis was applied to explore interrelationships among

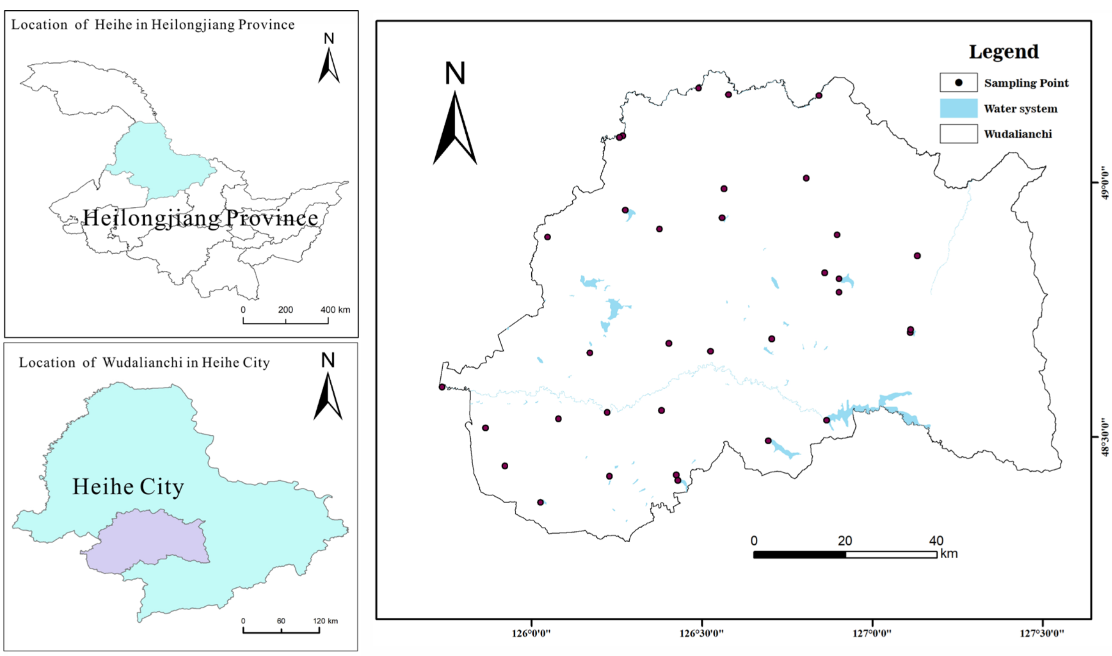

Figure 1. Study areas and sampling site

different chemical indicators and identify key factors influencing groundwater hydrochemical characteristics. Concurrently, the Schukalev classification scheme was employed to determine hydrochemical facies based on milliequivalent percentage (%meq) of anions and cations. Additionally, Durov diagrams, Gibbs models, and ion ratio analysis were utilized to further interpret the causes and spatial distribution patterns of groundwater hydrochemical characteristics.[31-33]

2.3.2. Water quality evaluation method: Entropy-weighted Water Quality Index

The water quality index constitutes a category of environmental quality indices, representing a dimensionless value that comprehensively describes water quality by integrating test results from multiple water quality parameters.

To objectively reflect the relative contributions of different hydrochemical indicators in water quality evaluation, the entropy weight method was introduced[34], which determines the entropy indices based on data deviation to calculate indicator weights. This approach determines entropy values according to the degree of data variation and computes the weight of each indicator, forming the EWQI.[35,36] The computational steps of EWQI are as follows[37-42]:

(a) Step 1

According to the number of determined samples n and indicators m, the original data matrix X is constructed, as shown in **Equation 1**:

$$X = \begin{pmatrix} x_{11} & x_{12} & \cdots & x_{1n} \\ x_{21} & x_{22} & \cdots & x_{2n} \\ \vdots & \vdots & & \vdots \\ x_{m1} & x_{m2} & \cdots & x_{mn} \end{pmatrix} \left(x_{ij}, i = 1,2,\ldots,nj = 1,2,\ldots,m\right) \tag{1}$$

(b) Step 2

Standardize each indicator to eliminate the influence of different units, characteristic indicators, and quality categories. Since all j-th indicators are negative indicators, **Equation 2** is commonly used for positive transformation to construct a standardized matrix Y, as shown in **Equation 3**.

$$y_{ij} = \frac{\left(x_{ij}\right)_{max} - x_{ij}}{\left(x_{ij}\right)_{max} - \left(x_{ij}\right)_{min}} \tag{2}$$

$$Y = \begin{pmatrix} y_{11} & y_{12} & \cdots & y_{1n} \\ y_{21} & y_{22} & \cdots & y_{2n} \\ \vdots & \vdots & & \vdots \\ y_{m1} & y_{m2} & \cdots & y_{mn} \end{pmatrix} \tag{3}$$

(c) Step 3

Calculate the proportion of the i-th sample under the j-th indicator, where Pij is the proportion of the i-th sample in the j-th indicator, as shown in **Equation 4**:

$$P_{ij} = \frac{y_{ij}}{\sum_{i=1}^{m} y_{ij}}, \quad i = 1,2,\ldots,n; j = 1,2,\ldots,m \tag{4}$$

(d) Step 4

The entropy weight parameter is expressed using **Equation 5**.

$$e_j = -\frac{1}{\ln m} \sum_{i=1}^{m} P_{ij} \cdot lnP_{ij} \tag{5}$$

(e) Step 5

Determine the weight of each indicator through using **Equation 6**.

$$w_j = \frac{1 - e_j}{\sum_{j=1}^{n}\left(1 - e_j\right)} \tag{6}$$

(f) Step 6

Calculate the graded quantitative standard for each indicator, as shown in **Equation 7**:

$$q_j = \frac{C_j}{S_j} \times 100 \tag{7}$$

where C_j is the measured concentration of hydrochemical ions in the sample (mg·L^{-1}), and S_j is the ion concentration specified in the "Standard for Groundwater Quality (GB/T 14848-2017)".

(g) Step 7

The calculation formula of EWQI is shown in **Equation 8**:

$$EWQI = \sum_{j=1}^{n}\left(w_j \bullet q_j\right) \tag{8}$$

Based on the EWQI results, groundwater quality is classified into five grades (Table 1), ranging from excellent to extremely poor (I–V). Among them, Grade I and II water are suitable for direct drinking, Grade III water needs to be treated and processed before drinking, and Grade IV and V water are suitable for agricultural and industrial use.

2.3.3. Health risk assessment model

The Human Health Risk Assessment model established by the USEPA is widely used to evaluate the potential harmful effects of groundwater pollutants on human health.[43-45] Polluted water can pose risks to human health mainly through direct oral intake and skin contact. Given that groundwater in the study area is predominantly used for drinking (>90% of household water use), and dermal/inhalation exposures during bathing or irrigation are minimal under local cold-climate usage patterns, this study follows USEPA Tier 1 screening principles to focus on the non-carcinogenic health risks caused by pollutants through direct drinking water. **Equations 9–11** were used to calculate the non-carcinogenic health risk assessment based on exposure via direct oral intake of pollutants.

$$CDI = \frac{C_w \times IR \times EF \times ED}{BW \times AT} \quad (9)$$

$$HQ_i = \frac{CDI}{RfD} \quad (10)$$

$$HI = \sum HQ_i \quad (11)$$

where:

(i) CDI = Chronic daily intake of pollutants through drinking water (mg·[kg·d]$^{-1}$).
(ii) C_w = Concentration of pollutants in water (mg·L^{-1}).
(iii) IR = Daily intake of groundwater (L·d^{-1}).
(iv) EF = Exposure frequency (d·a^{-1}).
(v) ED = Exposure duration (a).
(vi) BW = Average body weight (kg).
(vii) AT = Average time (d).
(viii) HQ_i = Non-carcinogenic health risk index of a single pollutant.
(ix) RfD = Reference dose of pollutants (mg·[kg·d]$^{-1}$).
HI = Hazard index, defined as the sum of hazard quotients

The parameters are shown in Table 2.

The health risk value of non-carcinogens in groundwater through drinking water pathways was calculated. According to the USEPA health risk evaluation criteria, the reference threshold value of the non-carcinogenic hazard index (HI) is 1. When HI < 1, the potential risk is negligible; when HI is in the range of 1–4, it indicates a moderate potential risk; when HI > 4, it indicates a high potential risk.

2.4. Sensitivity analysis

The Morris screening method[29] was employed to identify the key parameters that significantly influence the HI within the health risk assessment model. The parameters (C_w, IR, EF, ED, BW, AT, and RfD) were varied by ±10%, and the resulting percentage change in HI was calculated to assess

Table 1. Classification of Entropy-weighted Water Quality Index

EWQI	Grade	Water quality
≤50	I	Excellent
51–100	II	Good
101–150	III	Moderate
151–200	IV	Poor
>200	V	Extremely poor

Abbreviation: EWQI: Entropy-weighted Water Quality Index.

Table 2. Parameters of health risk assessment model

Parameter	Unit	Adults	Children
Concentration of pollutants in water (C_w)	mg·L^{-1}	Measured	Measured
Daily intake of groundwater (IR)	L·d^{-1}	1.8	0.7
Exposure frequency (EF)	d·a^{-1}	365	365
Exposure duration (ED)	a	24	6
Average body weight (BW)	kg	61.8	19.2
Average time (AT)	d	8,760	2,190
Reference dose of pollutants (RfD)	mg·(kg·d)$^{-1}$	1.6	1.6

Note: Exposure parameters for different populations were obtained from *Highlights of the Chinese Exposure Factors Handbook*, and reference dose of pollutants values were obtained from the United States Environmental Protection Agency Integrated Risk Information System.[46-48]

the importance of each parameter. The reference HI value for each sampling point was determined using the original parameter values, followed by a ±10% variation applied individually to each parameter to evaluate sensitivity.

$$\text{Sensitivity coefficient} = \frac{\dfrac{HI_{change} - HI_{baseline}}{HI_{baseline}}}{\text{Percentpage change in parameter}} \quad (12)$$

3. Results and discussion

3.1. Basic hydrochemical characteristics of groundwater

SPSS Statistics version 26 was utilized for statistical analysis of conventional indicators in water samples, and the results are shown in Table 3. The statistical results indicate that the pH value of groundwater in the study area ranges from 5.87 to 8.10, with a mean of 7.07, generally ranging from weakly acidic to weakly alkaline, and the exceedance rate is 17.66%. The TDS ranges from 27.75 to 515.40 mg/L, with a mean of 129.55 mg/L, which is lower than the limit value of 1,000 mg/L, indicating that the groundwater in the study area is classified as low-mineralization freshwater.

The order of average concentrations of major cations is: Ca^{2+} (35.59 mg/L) > Na^+ (23.97 mg/L) > Mg^{2+} (10.46 mg/L) > K^+ (5.60 mg/L).

The order of average concentrations of major anions is: HCO_3^- (107.44 mg/L) > Cl^- (44.73 mg/L) > NO_3^- (39.66 mg/L) > SO_4^{2-} (23.78 mg/L). Among them, the exceedance rate of NO_3^- is as high as 35.29%, indicating that some areas have been significantly affected by anthropogenic pollution.[49-51]

The coefficient of variation can intuitively reflect the variation of ions in groundwater. As shown in Table 3, the coefficient of variation of pH is less than 0.1, indicating weak variation, suggesting that the acidity and alkalinity of groundwater in the Wudalianchi area remain relatively stable and less affected by external disturbances; the coefficients of variation of Na^+, K^+, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-} are all greater than 1, indicating that these ions have complex spatial distributions in groundwater, with diverse sources of chemical components and high possibility of being affected by human activities; the coefficients of variation of other ions are between 0.1 and 1, indicating moderate variation, meaning these ion components are relatively stable.

Table 3. Statistics of groundwater hydrochemical components

Indicator	Minimum	Maximum	Mean	Standard deviation	Coefficient of variation	Limit value	Exceedance rate (%)
pH	5.87	8.10	7.07	0.64	0.09	6.5–8.5	17.66
TH	32.54	499.59	137.53	117.41	0.85	450	2.9
TDS	27.75	515.40	129.55	111.53	0.86	1,000	0
Na^+	3.25	124.92	23.97	26.83	1.12	200	0
K^+	0.58	61.83	5.60	10.88	1.94	200	0
Mg^{2+}	1.59	45.71	10.46	11.37	1.09	50	0
Ca^{2+}	9.42	131.62	35.59	28.65	0.81	400	0
Cl^-	0.72	179.87	44.73	52.86	1.18	250	0
NO_3^-	1.23	191.28	39.66	59.02	1.49	20	35.29
SO_4^{2-}	3.26	180.82	23.78	40.12	1.69	250	0
HCO_3^-	30.02	300.24	107.44	66.49	0.62	450.00	0

Note: The unit of concentration for each parameter is $mg \cdot L^{-1}$, except for pH, which is dimensionless. The limit value reference is taken from the Standards for Drinking Water Quality (GB 5749-2022).[52]
Abbreviations: TDS: Total dissolved solids; TH: Total hardness.

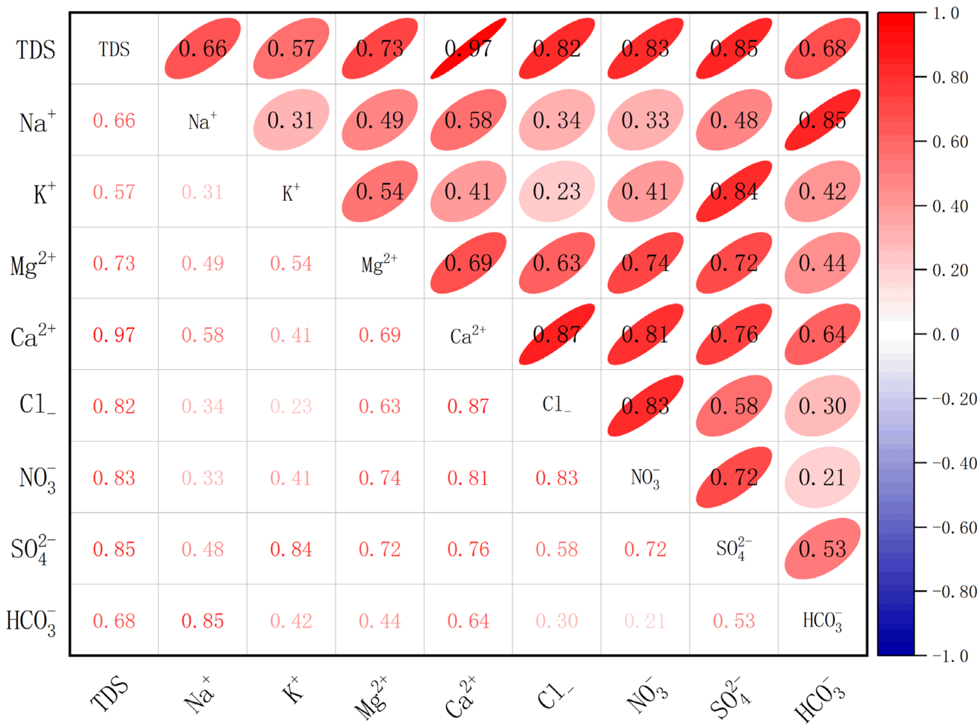

Figure 2. Correlation of groundwater quality in the study area. $^*p < 0.05$, $^{**}p < 0.01$, and $^{***}p < 0.001$ indicate statistical significance.

3.2. Correlation of groundwater components

Correlation analysis of groundwater chemical indicators (Figure 2) constitutes an important approach to unraveling geochemical processes and water quality controlling factors.[53-56] This investigation employed groundwater chemical data from Wudalianchi County for correlation analysis. The correlation coefficient ranges from −1 to 1, where a positive value indicates a positive correlation, a negative value indicates a negative correlation, and the closer the absolute value is to 1, the stronger the correlation.

The correlation heatmap of groundwater chemical data in the study area shows that TDS is significantly positively correlated with all ions, indicating that these ions are the dominant contributors to the mineralization of water in the study area. TDS has the highest correlation with Ca^{2+}, close to 1 ($r = 0.97$, $p < 0.001$), showing a very strong positive correlation, indicating that Ca^{2+} is the key ion controlling mineralization. It also shows a very strong positive correlation with Cl^- ($r = 0.82$, $p < 0.001$), NO_3^- ($r = 0.83$, $p < 0.001$), and SO_4^{2-} ($r = 0.85$, $p < 0.001$), which are important auxiliary contributors to TDS, further indicating the superimposed influence of anthropogenic inputs on mineralization.

There is an extremely significant positive correlation between Ca^{2+} and Mg^{2+} ($r = 0.69$, $p < 0.001$), indicating that they may have a common source in water; HCO_3^- has a very strong positive correlation with Na^+ ($r = 0.85$, $p < 0.001$), which is presumably related to the dissolution of sodium-bearing minerals, forming a key "cation–anion" pair in water. K^+ has a very strong positive correlation with SO_4^{2-} ($r = 0.84$, $p < 0.001$), which may originate from the dissolution of sulfate minerals. Other cations have weak and insignificant correlations, indicating large differences in their respective sources or migration paths. Cl^- has an extremely significant strong positive correlation with NO_3^- ($r = 0.83$, $p < 0.001$), which may be related to agricultural activities or domestic sewage discharge, and the pollution sources of the two are highly consistent. Cl^- has an extremely significant strong positive correlation with Ca^{2+} ($r = 0.87$, $p < 0.001$), and NO_3^- has a very strong positive correlation with Ca^{2+} ($r = 0.81$, $p < 0.001$). Combined with cation analysis, this indicates that Cl^-, NO_3^-, Ca^{2+}, and Mg^{2+} together form the main ion combination in water, which may originate from the synergistic dissolution of carbonate rocks and nitrogen- or chlorine-containing substances.

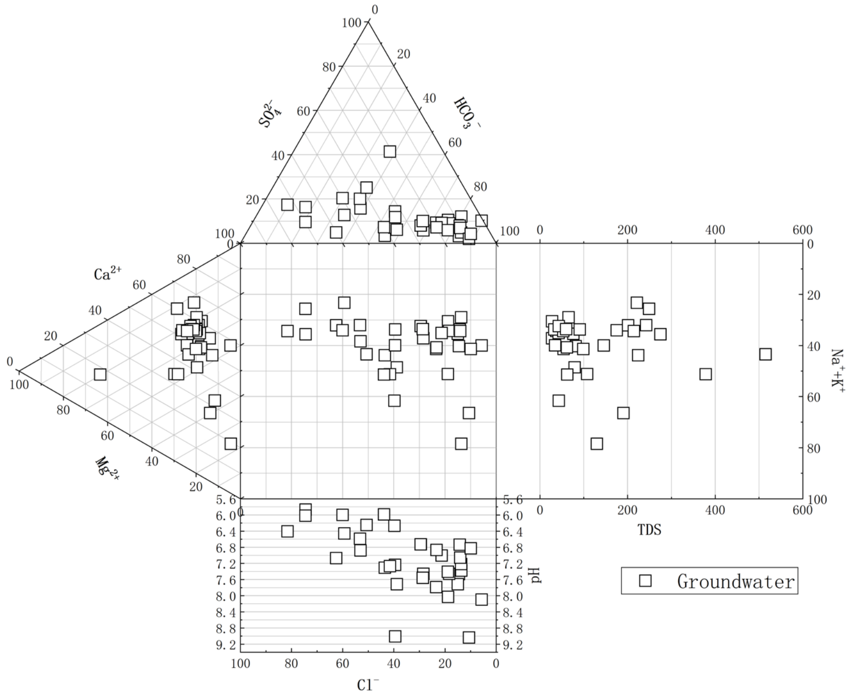

Figure 3. Durov diagram of groundwater
Abbreviation: TDS: Total dissolved solids.

3.3. Characteristics of groundwater hydrochemical types

To determine the groundwater hydrochemical types in Wudalianchi County, the main groundwater ions—including Ca^{2+}, Mg^{2+}, $K^{+}+Na^{+}$, Cl^{-}, SO_4^{2-}, HCO_3^{-}—pH, and TDS were plotted into a Durov diagram. As shown in Figure 3, in the cation triangular diagram, more than 90% of the sampling points are concentrated near the Ca^{2+} vertex, making it the dominant cation, with local supplementation of $K^{+}+Na^{+}$. In the anion triangular diagram, most sampling points are far from the Cl^{-} vertex, and, combined with the previous data that HCO_3^{-} accounts for a high proportion, HCO_3^{-} is judged to be the dominant anion. The hydrochemical types in the study area are mainly HCO_3^{-}Ca and HCO_3^{-}Ca·Na, with HCO_3–Ca as the core ion combination.

3.4. Analysis of causes of hydrochemical characteristics

The formation of groundwater hydrochemical characteristics is controlled by three processes: atmospheric precipitation, rock weathering, and evaporation–concentration. The core function of the Gibbs diagram is to determine the chemical genesis type and control evolution process of natural water bodies by correlating the main ion composition of water (such as cations $Na^{+}+K^{+}$, Ca^{2+}, and Mg^{2+}, and anions Cl^{-}, SO_4^{2-}, and $HCO_3^{-}+CO_3^{2-}$) with TDS, and to trace the recharge source. This is a common method for analyzing hydrochemical evolution characteristics.[57-59]

As shown in Figure 4A, the sample points are relatively scattered, but most of the $Cl^{-}/(Cl^{-}+HCO_3^{-})$ values are concentrated in the range of 0–0.6, and TDS is mainly distributed between 10–1,000 mg·L^{-1}. Most points fall in the rock weathering zone, indicating that the chemical composition of groundwater in the study area is mainly controlled by rock weathering.

In Figure 4B, most water samples fall in the rock weathering control zone, and a few water samples are distributed near the evaporation–concentration control zone. Specifically, the TDS corresponding to anions and cations is mainly concentrated in the medium-low mineralization range of 100–800 mg·L^{-1}, and all sample points fall into the "rock weathering type" zone. Only 2–3 sample points are close to the "precipitation-controlled type" boundary, presumably because shallow groundwater is more significantly affected by atmospheric precipitation

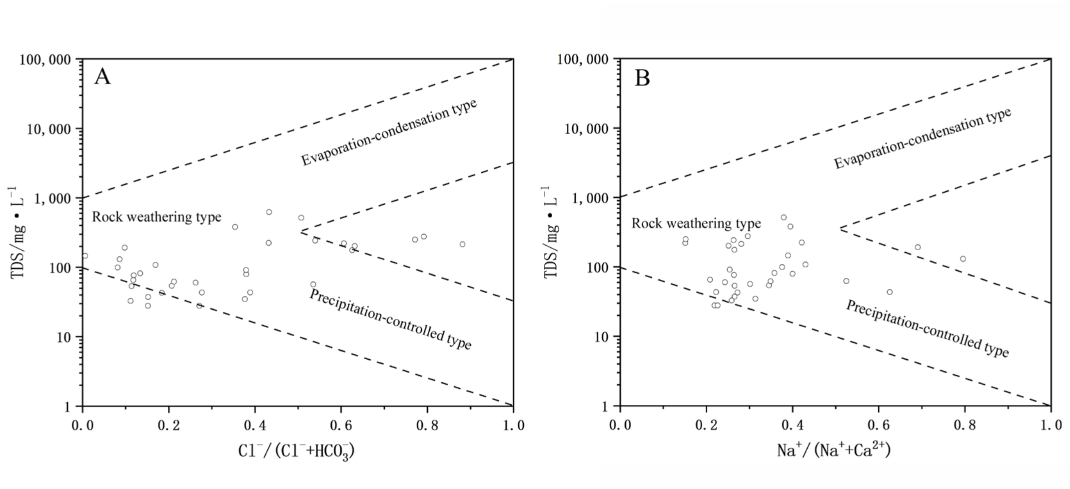

Figure 4. Gibbs diagram of groundwater chemistry. (A) Anion dominance plot (TDS vs. $Cl^-/[Cl^- + HCO_3^-]$). (B) Cation dominance plot (TDS vs. $Na^+/[Na^+ + Ca^{2+}]$).
Abbreviation: TDS: Total dissolved solids.

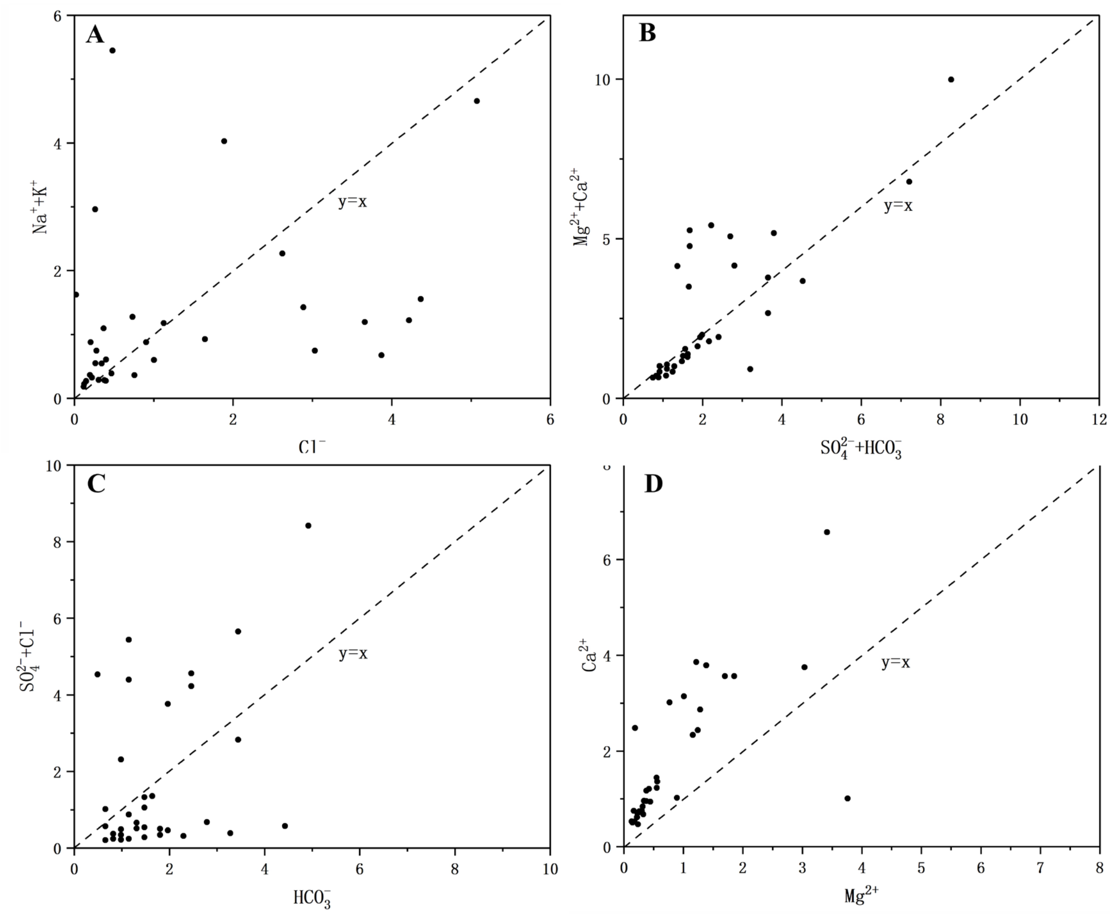

Figure 5. Ion coefficient relationship diagrams. (A) $(Na^+ + K^+)$ vs. Cl^-. (B) $(Mg^{2+} + Ca^{2+})$ vs. $(SO_4^{2-} + HCO_3^-)$. (C) $(SO_4^{2-} + Cl^-)$ vs. HCO_3^-. (D) Ca^{2+} vs. Mg^{2+}.

recharge, with relatively lower TDS. No sample points fall into the "evaporation–concentration type," reflecting that the study area has a humid climate and a fast groundwater circulation rate, and the enrichment effect of evaporation on hydrochemical composition is weak.

The ion ratio coefficient method reflects the ratio of milliequivalents of ions in a rectangular coordinate system. Based on the coefficient value, it judges the source of groundwater chemical components, analyzes the causes of groundwater chemistry, and thereby reveal the formation process and mechanism of regional groundwater.[60]

Figure 5A shows the relationship between Na^{+}+K^{+} and Cl^{-}. Most points fall below the dashed line, indicating that the equivalent of Na^{+}+K^{+} is lower than that of Cl^{-}. This indicates that Na^{+} + K^{+} in the groundwater not only comes from halite dissolution but also undergoes cation exchange or K^{+} adsorption by clay minerals, resulting in a deviation of its actual content from the ideal value of halite dissolution.

In Figure 5B, most points are close to the dashed line, indicating that Ca^{2+} and Mg^{2+} in the groundwater mainly originate from the dissolution of carbonate and sulfate minerals, which is the core process controlling the cation composition. The points in Figure 5C are highly scattered, indicating complex sources of anions: HCO_3^{-} mainly comes from carbonate dissolution, while SO_4^{2-} and Cl^{-} may come from sulfate mineral dissolution, halite dissolution, or human activities. The proportion of anion sources varies greatly among different sampling points, leading to no stable equivalent relationship between them.

As shown in Figure 5D, most points fall below the dashed line, which is related to the mineral composition of the aquifer. Dissolution will increase the Mg^{2+} content; it may also be that Ca^{2+} forms calcium carbonate precipitation, further reducing the Ca^{2+} concentration in water.

The ratio results of (Ca^{2+} Mg^{2+})/(HCO_3^{-} SO_4^{2-}) and (Na^{+} K^{+})/Cl^{-} indicate that the dissolution of volcanic-derived silicate minerals (e.g., feldspar and pyroxene) released Ca^{2+}, Mg^{2+}, and HCO_3^{-}, which is consistent with the main HCO_3–Ca water type.

3.5. Water quality and health risk assessment

In this study, a total of 11 relevant parameters from the water quality data, including TDS, TH, pH, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, NO_3^{-}, SO_4^{2-}, and HCO_3^{-}, were selected as water

Table 4. Hydrochemical weights based on Entropy-weighted Water Quality Index

Indicator	pH	TH	TDS	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	Cl^{-}	NO_3^{-}	SO_4^{2-}	HCO_3^{-}
Entropy value	0.99	0.98	0.98	0.98	0.99	0.98	0.98	0.97	0.97	0.98	0.98
Difference coefficient	0.01	0.02	0.02	0.02	0.01	0.02	0.02	0.03	0.03	0.02	0.02
Weight	0.04	0.10	0.08	0.07	0.05	0.11	0.08	0.14	0.14	0.08	0.11

Abbreviations: TDS: Total dissolved solids; TH: Total hardness.

Table 5. Classification of groundwater quality based on the Entropy-weighted Water Quality Index

EWQI grade	Water quality level	Number of samples	Proportion (%)
≤50	Excellent	25	70.59
51–100	Good	3	8.82
101–150	Moderate	6	17.65
151–200	Poor	1	2.94
>200	Extremely poor	0	0
Total	–	34	100

Note: The EWQI range of all samples is 5.87–197.37, with an average value of 44.01.
Abbreviation: EWQI: Entropy-weighted Water Quality Index.

quality evaluation indicators from the 34 collected water samples. The EWQI was used to evaluate the groundwater quality.

As shown in Table 4, the weights of each indicator in the water quality evaluation of the study area are: NO_3^- > Cl^- > Mg^{2+} > HCO_3^- > TH > TDS > Ca^{2+} > SO_4^{2-} > Na^+ > K^+ > pH. Among them, NO_3^- has the highest weight of 0.14, indicating that NO_3^- plays a leading role in EWQI in groundwater quality evaluation, while pH has the lowest weight of 0.04, indicating its relatively minor influence on groundwater quality in the study area.

The EWQI values of groundwater in the study area range from 5.87 to 197.37, with an average of 44.01. The detailed classification statistics are listed in Table 5.Among them, 25 water samples are classified as excellent water quality, accounting for 70.59% of the total samples, representing the largest proportion—three water samples are classified as good water quality, accounting for 8.82%; six water samples are classified as moderate water quality, accounting for 17.65%; and one water sample is classified as poor water quality, accounting for 2.94%. There are no water samples with extremely poor water quality. Overall, the groundwater quality in the study area is relatively good.

The dominance of NO_3^- weight (0.14) and its exceedance rate (35.29%) suggest that anthropogenic inputs (fertilizers, sewage) are the primary threat to drinking water safety. The spatial pattern of EWQI (Figure 6) indicates that excellent water quality is mainly distributed in the eastern forest areas, while moderate-to-poor quality appears in the western urban and industrial zones.

The NO_3^- indicator with an exceedance rate of 35.29% in the groundwater of the study area was selected for human health risk evaluation, and the HQ values of groundwater parameters were calculated using **Equations 9** and **10**.[60-63]

According to the evaluation model established by the USEPA, this study analyzed the impact of NO_3^- on human health risks. The results are shown in Table 6. The non-carcinogenic health risks of NO_3^- to children through

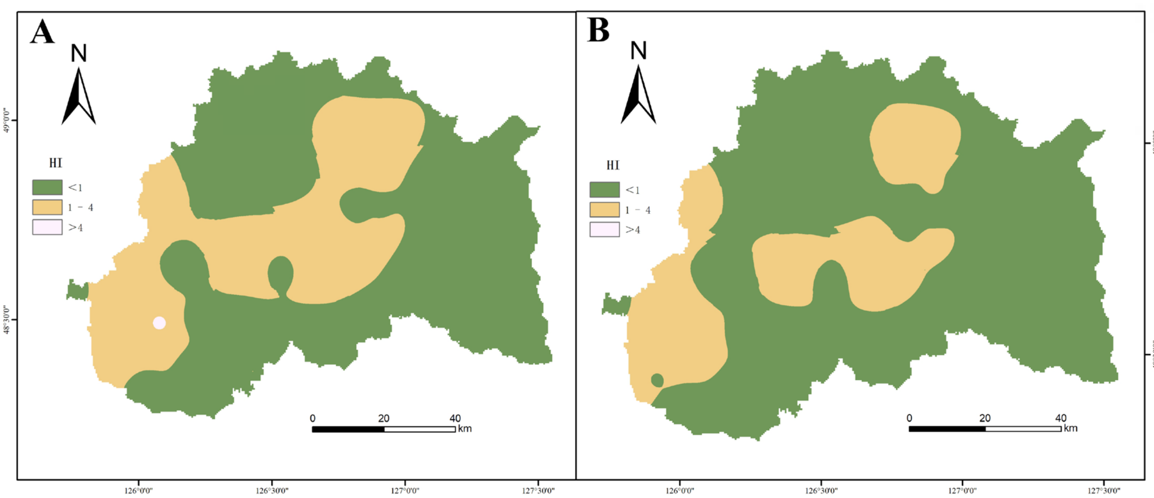

Figure 6. Spatial distribution map of groundwater hazard index (HI) in the study area: (A) Children; (B) adults

Table 6. Statistical summary of non-carcinogenic risks of groundwater in the study area

Population	Hazard index			
	Minimum	Maximum	Average	Exceedance proportion
Children	0.03	4.36	0.90	29.41%
Adults	0.02	3.48	0.72	23.53%

drinking water pathways range from 0.03 to 4.36, with an average of 0.90, and the proportion of samples exceeding the acceptable range reaches 29.41%. The non-carcinogenic health risks to adults ranged from 0.02 to 3.48, with an average of 0.72, and the proportion of samples exceeding the acceptable range reaches 23.53%.

Among the 34 sampling points, eight points have excessive HQ values for adults and 10 points have excessive HQ values for children. Moreover, the HQ values for children at all points are higher than those for adults, with an average increase of about 25%. In the same groundwater environment, children are more vulnerable to harm than adults[64], which is related to children's lower body weight and immature metabolic systems.[65-67]

Interpolation analysis was performed on the non-carcinogenic health risk values, as shown in Figure 6. Most of the groundwater samples exceeding the acceptable threshold are distributed in the western part of the study area, which is the urban area and industrial concentration zone of Wudalianchi County. Nitrate mainly comes from agricultural activities, urban and industrial discharge, solid waste disposal, and natural geological background sources. There is only one water sample point in the area with HI > 4, which is located on the edge of Wudalianchi County's urban area—a residential area. It is speculated that the increase in groundwater nitrate is caused by domestic sewage or poultry manure discharge. The health risk index in most other areas is less than 1, which also confirms that areas such as the eastern part of the study area are farms, forest farms, and other areas with minimal anthropogenic influence.

The sensitivity analysis presented in Table 7 demonstrates that the sensitivity ranking and change rates of all parameters are consistent across both children and adults. *BW*, *AT*, and *RfD* exert the most significant influence on the HI, exhibiting an absolute average change rate of 10.10%. The sensitivity of all parameters approaches 10%, suggesting that HI is relatively responsive to variations in each parameter. Furthermore, the sensitivity of inversely proportional parameters is marginally greater than that of directly proportional parameters.

Compared with volcanic aquifers reported from Ethiopia, Indonesia, Tanzania, and other regions, the Wudalianchi groundwater system shows similar evidence of water–rock interaction and ion exchange, but the main public-health concern is driven by localized nitrate contamination rather than fluoride enrichment or salinity. In the Yogyakarta–Sleman basin and the Hong Kong volcanic rock hillslope, spatial heterogeneity and mixing processes are the dominant controls on groundwater chemistry.[12,16]

In the Axum volcanic area and the Meru volcanic complex, mineral dissolution and fluoride-related geochemical processes are the primary issues affecting groundwater quality.[13,14] In contrast, the Wudalianchi groundwater system is characterized by generally low-mineralization Ca–HCO_3 type water, but with significant NO_3^- enrichment in the western urban and agricultural zones, making anthropogenic input the key factor driving local water quality deterioration and health risk. These

Table 7. Sensitivity analysis ranking

Ranking	Parameter	Sensitivity in children	Sensitivity in adults	Category	Difference
1	Average body weight (*BW*)	10.10%	10.10%	Inverse parameter	Same
2	Average time (*AT*)	10.10%	10.10%	Inverse parameter	Same
3	Reference dose of pollutants (*RfD*)	10.10%	10.10%	Inverse parameter	Same
4	Concentration of pollutants in water ($C_{w)}$	10.00%	10.00%	Direct parameter	Same
5	Daily intake of groundwater (*IR*)	10.00%	10.00%	Direct parameter	Same
6	Exposure frequency (*EF*)	10.00%	10.00%	Direct parameter	Same
7	Exposure duration (*ED*)	10.00%	10.00%	Direct parameter	Same

comparisons indicate that groundwater evolution in volcanic aquifers is highly site-specific and is controlled by the interplay of volcanic lithology, recharge conditions, hydrogeological structure, and land use. Therefore, the present study provides an important case from a cold-temperate volcanic county in Northeast China and complements the global literature on volcanic groundwater hydrochemistry and health risk assessment.

3.6. Limitations and perspectives

This study has three limitations:

(i) Sampling was only conducted during the rainy season, and the seasonal variations in water chemical characteristics and health risks require long-term monitoring.
(ii) Isotope tracing (e.g., $\delta^{15}N–NO_3^-$, $\delta^{18}O–NO_3^-$) was not used to distinguish the sources of NO_3^-.
(iii) Only the oral intake route was considered in this study.

Future studies should include the risks of skin contact and inhalation. Future research should also combine isotope and microbial indicators to track the sources of pollutants, carry out long-term dynamic monitoring of groundwater and surface water, to reveal hydrological connectivity, and integrate predictive models and machine learning in order to predict groundwater quality trends.

4. Conclusion

Groundwater hydrochemistry in the study area is governed by water–rock interaction processes in volcanic aquifer minerals. Dissolution of volcanic silicate minerals (e.g., feldspar, pyroxene) and carbonate minerals releases large amounts of Ca^{2+}, Mg^{2+}, and HCO_3^-, which fundamentally determines the dominant HCO_3–Ca and HCO_3–Ca·Na hydrochemical types. The regional groundwater belongs to low-mineralization freshwater, and the overall hydrochemical composition is stable under natural geological conditions.

Additionally, nitrate pollution is the key factor deteriorating groundwater quality and inducing health risks. The nitrate over-limit rate reaches 35.29%, and its weight in EWQI ranks the highest among all indices. Excess nitrate originates from agricultural fertilization and domestic sewage discharge in western urban and industrial zones. The non-carcinogenic risks of nitrate exceed safety thresholds in 29.41% of samples for children and 23.53% for adults, proving that anthropogenic activities have severely disturbed the local groundwater environment.

Moreover, children suffer approximately 25% higher health risks than adults exposed to the same groundwater environment. This discrepancy is primarily driven by physiological differences: children have lower body weight, higher water intake per unit weight, and incomplete development of liver and renal metabolic functions, resulting in reduced pollutant tolerance and higher health vulnerability compared with adults.

Collectively, this study provides solid scientific support for groundwater protection and drinking water safety management in Wudalianchi County, and fills the research gap of systematic hydrochemical and health risk assessment in cold-temperate volcanic regions. Given the limitations of single-season sampling and single exposure pathway assessment in this work, long-term dynamic monitoring, multi-source nitrate identification via isotopic tracers, and multi-pathway health risk simulation should be carried out in follow-up studies to support sustainable groundwater management and pollution prevention.

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Conflict of interest

The authors have no relevant financial or non-financial interests to disclose.

Author contributions

Conceptualization: All authors
Data curation: Jiajia Xu, Haonan Song
Methodology: Youtao Xin
Resources: Zhongkai Liang
Software: Youtao Xin, Jiajia Xu, Haonan Song
Validation: Jiajia Xu
Visualization: Jiajia Xu, Haonan Song
Writing–original draft: Youtao Xin
Writing–review & editing: Zhongkai Liang

Availability of data

Data are available from the corresponding author upon reasonable request.

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