Journal of Groundwater Science and Engineering
ISSN 2305-7068
Indexed by ESCI CABI CSA Scopus GeoRef AJ CNKI

Spatial-temporal difference between nitrate in groundwater and nitrogen in soil based on geostatistical analysis

Xiu-bo Sun, Chang-lai Guo, Jing Zhang, Jia-quan Sun, Jian Cui, Mao-hua Liu

Citation:
Sun XB, Guo CL, Zhang J, *et al*. 2023. Spatial-temporal difference between nitrate in groundwater and nitrogen in soil based on geostatistical analysis. Journal of Groundwater Science and Engineering, 11(1): 37-46.

View online: https://doi.org/10.26599/JGSE.2023.9280004

Journal homepage: http://gwse.iheg.org.cn

Spatial-temporal difference between nitrate in groundwater and nitrogen in soil based on geostatistical analysis

Xiu-bo Sun[1], Chang-lai Guo[1], Jing Zhang[1], Jia-quan Sun[1], Jian Cui[1*], Mao-hua Liu[2]

[1] *Shenyang Center of Geological Survey*, *CGS*, *Shengyang* 110000, *China*.
[2] *Shenyang Jianzhu University*, *Shengyang* 110168, *China*.

Abstract: The study of temporal and spatial variations of nitrate in groundwater under different soil nitrogen environments is helpful to the security of groundwater resources in agricultural areas. In this paper, based on 320 groups of soil and groundwater samples collected at the same time, geostatistical analysis and multiple regression analysis were comprehensively used to conduct the evaluation of nitrogen contents in both groundwater and soil. From May to August, as the nitrification of groundwater is dominant, the average concentration of nitrate nitrogen is 34.80 mg/L; The variation of soil ammonia nitrogen and nitrate nitrogen is moderate from May to July, and the variation coefficient decreased sharply and then increased in August. There is a high correlation between the nitrate nitrogen in groundwater and soil in July, and there is a high correlation between the nitrate nitrogen in groundwater and ammonium nitrogen in soil in August and nitrate nitrogen in soil in July. From May to August, the area of low groundwater nitrate nitrogen in 0–5 mg/L and 5–10 mg/L decreased from 10.97% to 0, and the proportion of high-value area (greater than 70 mg/L) increased from 21.19% to 27.29%. Nitrate nitrogen is the main factor affecting the quality of groundwater. The correlation analysis of nitrate nitrogen in groundwater, nitrate nitrogen in soil and ammonium nitrogen shows that they have a certain period of delay. The areas with high concentration of nitrate in groundwater are mainly concentrated in the western part of the study area, which has a high consistency with the high value areas of soil nitrate distribution from July to August, and a high difference with the spatial position of soil ammonia nitrogen distribution in August.

Keywords: Groundwater; Nitrate; Soil; Spatial-temporal variation; Geostatistical analysis

Received: 12 Apr 2022/ Accepted: 26 Dec 2022/ Published: 20 Mar 2023

Introduction

The continuous increase of nitrate nitrogen (NO_3^--N) content in water has become one of the main environmental problems taking place in many countries. In many areas of China, nitrate pollution commonly presents in shallow groundwater. The high content of nitrate has led to the overload of groundwater environmental carrying capacity (E Sacchi et al. 2013; Abdelhakim, 2020; Sun et al. 2022). Furthermore, excessive nitrate poses a serious threat to aquatic ecosystem and human health (Pati et al. 2014; Michener and Lajtha, 2007; Zhang et al. 2014; Li et al. 2019), Cui et al. (2022) analyzed the trend of nitrate against the change of land use in the future, from which they stated that the nitrate concentration might have an increasing trend with the increase of cultivated land area in the next 30 years. Scientists have jointly applied the methods of nitrate and oxygen isotope, and other methods to the research of groundwater nitrate pollution traceability (Ma et al. 2021; Yuan et al. 2022; Li et al. 2022). To get a better understanding of the source of groundwater nitrogen, Huang shuang carried out a simulation of nitrate peak migration time in the global vadose zone based on GIS, and analyzed when the nitrate peak reached groundwater level (Huang. 2019).

Geostatistics is a random variable model based on the spatial correlation of sampling points. Based on regionalized variables, geographical phenomena with spatial correlation and dependence are studied by means of variogram, and the best unbiased interpolation estimation is made on the sample data

*Corresponding author: Jian Cui, *E-mail address*: spidercj@126.com

DOI: 10.26599/JGSE.2023.9280004

Sun XB, Guo CL, Zhang J, et al. 2023. Spatial-temporal difference between nitrate in groundwater and nitrogen in soil based on geostatistical analysis. Journal of Groundwater Science and Engineering, 11(1): 37-46.

to simulate the correlation and variability of spatial distribution of the geographical phenomena. This method not only explains the influence of natural factors and human activities on the spatial variation, but also reveals the spatial distribution and variation of random variables and related characteristics (Wang et al. 2020). Therefore, this paper comprehensively applied the methods of geostatistics and multiple regression analysis to study the spatial variations and temporal trends of nitrogen contents in groundwater and soil, with groundwater and soil samples collected in the period from May to August in northern Yixian County, Liaoning Province. Objective of this study is to assess groundwater nitrate pollution, and to understand the peak period, trend and temporal and spatial variations of the groundwater nitrogen in correspondence to those of soil nitrogen. The study will help provide guidance on soil nitrogen supply and rational application of nitrogen fertilizer, and will be helpful for dynamic monitoring and early warning research on groundwater carrying capacity.

1 Study area

The study area is located within 120°52′E–121°44′E and 41°17′N–41°48′N in the north of Yixian County, Liaoning Province. Yixian County is one of local municipalities with severe water shortage in Liaoning Province. The area has an average annual precipitation of 501 mm, of which the rainfall from May to October is 461.3 mm, accounting for 90% of the annual precipitation. The water resources are seriously insufficient, and droughts are frequent, with the probability of spring drought reaching 90%. The landform of the area is dominated by low hills, with hills and mountains accounting for 74% of the total area. Dendritic surface water system drains from the eastern and western hilly and mountainous areas to Daling River Valley Plain, with steep terrain slope and undeveloped vegetation. There are 1.4 million mu of cultivated land, mainly distributed in the valley plains and piedmont areas. Due to the arid climate, sparse vegetation, intense valley cutting and serious soil erosion in the area, the land is barren. In order to increase agricultural production and income, a large amount of fertilizer has been used in farming, which poses a certain threat to the groundwater environment.

2 Materials and methods

2.1 Data acquisition

In the study area, groundwater samples were collected mainly from irrigation wells and residence' water supply wells, and soil samples were collected near the cultivated land. The groundwater generally flows from north to south. There are 20 groundwater sampling points and 20 soil sampling points, respectively. The farthest distance between water and soil sampling point is 500 m, and the rest distances are less than 100 m. In May, June, July and August, 2021, 80 groups of groundwater samples were collected. There are 240 groups of soil profile samples (0–20 cm, 20–40 cm, 40–60 cm). The number of sample points is sufficient and the layout is reasonable (Fig. 1). The collected groundwater and soil samples were sent to Shenyang Geological Survey Center Laboratory of China Geological Survey for chemical constituent analyses. The concentration of nitrate was determined by phenol disulfonic acid colorimetry and ammonium by indophenol blue colorimetry, with no detection limit. The nitrate ion, nitrite ion and ammonium ion in groundwater were also detected. The detection limit of ammonia nitrogen was 0.026 mg/L by gas phase molecule, and the detection limits of nitrate ion and nitrite ion were 0.016 mg/L and 0.001 mg/L by ion chromatography, respectively.

2.2 Research methods

Geostatistical analysis determines the geographical location and distance of sample points through spatial data, and combines attribute data with spatial data to determine the relationship between step size and semi-variance function. In this paper, the geostatistical analysis method is mainly used to study the spatial variability of groundwater nitrate and soil, and the spatial autocorrelation between data sets is measured by semi-variation. The formula of semi-variation is:

$$\gamma(h) = \frac{1}{2}[z(x_i) - z(x_j)]^2 \quad (1)$$

Where: $\gamma(h)$ is the semivariation of the sum of known points; h indicating the distance between two points; and z is the attribute value. With the change of distance segment, a series of semivariogram values can be calculated. The semi-variation cloud map is established with h as abscissa and $\gamma(h)$ as ordinate. On the premise of spatial autocorrelation, the semi-variation between known points at short distance is small, while that between known points at long distance is large. According to the characteristics of semivariogram, a certain mathematical function or model must be used for fitting. In this study, most of them are sphere mo-

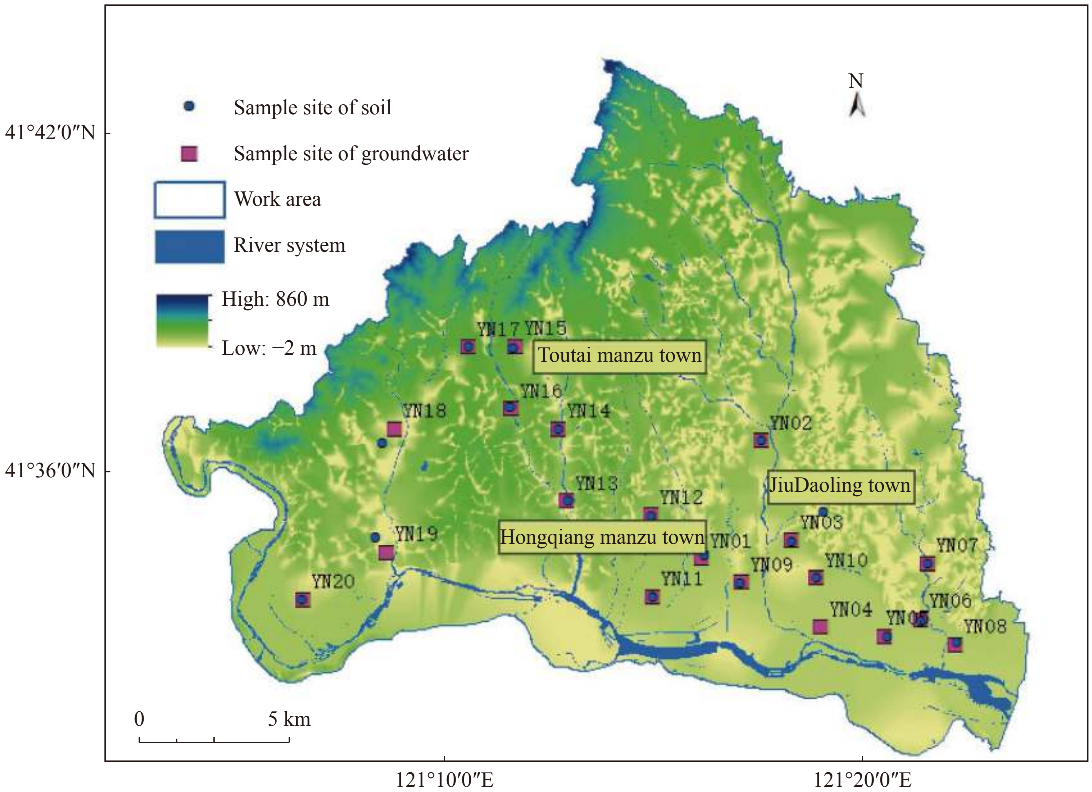


Fig. 1 Distribution of sample collection in work area

del and exponential model:

Sphere model:

$$\gamma(h) = C_0 + C\left[1.5\left(\frac{h}{a}\right) - 0.5\left(\frac{h}{a}\right)^3\right] \tag{2}$$

Exponential model:

$$\gamma(h) = C_0 + C\left(1 - e^{\frac{-h}{a}}\right) \tag{3}$$

Where: C_0 is the value of lump gold; $[C_0 + C]$ is the base station value; a for the range change. The nugget value C_0 indicates the size of random variation, and the base value $[C_0 + C]$ is the limit value of semivariogram. The ratio of nugget value to base value $[C_0/C_0 + C]$ is called nugget coefficient, which reflects the size of random variation in total variation. It is generally believed that when nugget coefficient is less than 0.25, the spatial correlation is strong; When the gold coefficient is 0.25–0.75, the spatial correlation is moderate; When the gold coefficient is greater than 0.75, the spatial correlation is weak. The range indicates the spatial continuity range of patches with similar properties. Within the range, the spatial variables have spatial autocorrelation or spatial dependence, but there is no spatial dependence outside the range (Dai et al. 2007).

Kriging, also known as spatial local estimation or spatial local interpolation, is one of the main components of geostatistical analysis. In essence, it is a method to make use of the original data of regionalized variables and the structural characteristics of variogram to estimate the value of the regionalized variables in the non-sampled points by linear unbiased optimization. Its advantage is that the estimation accuracy is higher than that of the common average method, which can avoid the occurrence of systematic errors and give the estimation error and accuracy (Zhang et al. 2022). This test adopts ordinary kriging interpolation method, and its calculation formula is:

$$Z(X_0) = \sum_{i=1}^{n} Z(X_i)\, w_i \tag{4}$$

Where: $Z(X_0)$ is the unknown sampling value; $Z(X_i)$ (i = 0, 1, 2, 3, ⋯, n) is the value of the known sampling point x_i; w_i is the weight coefficient. The weight coefficient here depends on the calculation result of the variogram, rather than simply determined by the distance.

3 Results and discussion

3.1 Statistical characteristics of nitrate in groundwater and soil

(1) Statistical characteristics of nitrate in groundwater

Nitrate (as NO_3^--N) is an important nitrogen species that affects groundwater quality in this area. The depths to water table of the shallow porous groundwater in the area are generally 1.19–11.67 m in dry season and 2.35–13.05 m in wet season. The groundwater samples collected in the four sampling rounds are all at the same point of Manmin well, and the sampling depth was 4–12 m. According to the Groundwater Quality Standard (GB/T 14848-2017), 80 groups of groundwater samples taken from the work area were evaluated and analyzed. Among the 80 groups of groundwater samples, the nitrate nitrogen contents of 51 groups or 63.75% exceed the acceptable level defined in the water quality standard (Table 1). The quality testing result shows that the nitrogen presents in the groundwater is mainly nitrate, accounting for 99.77% of total nitrogen content, whilst the nitrite and ammonium in groundwater account for 0.23% of total nitrogen in the groundwater.

For spatial data, the coefficient of variation less than 0.1 indicates a weak variability, 0.1–1 a medium variability and greater than 1 as strong variability (Ma et al. 2019). From May to August, 2021, the average nitrate contents of the four sampling rounds were 35.98 mg/L, 33.72 mg/L, 30.73 mg/L and 38.76 mg/L, respectively, with corresponding variation coefficients of 69.80%, 83.98%, 66.71% and 69.70%, which fall in a moderate variation range (Table 2). The average content and coefficient of variation of nitrate decreased at the first round and then increased. The coefficient of variation in May-August was close, indicating that the spatial variation in the year was not obvious. The average value of groundwater nitrate suddenly increased in August, showing that the concentration of NO^-_3-N (38.76 mg/L) was higher than that of the previous NO^-_3-N (35.98 mg/L).

(2) Statistical characteristics of nitrogen in soil

There are in total 240 groups of soil samples collected in the four sampling rounds for soil nitrate and ammonium analyses, with soil profile sampling depths at 0–20 cm, 20–40 cm and 40–60 cm, respectively. The variation trends of nitrate and ammonia nitrogen in the soils are plot in Fig. 2.

The contents of nitrate and ammonia nitrogen in different periods and depths of the soil change obviously. From May to July, the content of ammonium nitrogen in the soil was higher than that of nitrate nitrogen. In August, the content of ammonium nitrogen in the soil decreased obviously, and the content of nitrate nitrogen increased. At the soil profile, the contents of nitrate nitrogen and ammonium nitrogen decreased gradually with the increase of depth. In the soil at the same depth, the nitrate nitrogen content decreased obviously in the period of May-July, and increased obviously in August.

The statistical characteristics of soil nitrogen in the study area are shown in Table 3. From May to August 2021, the average values of soil ammonia nitrogen in the three profile layers were 17.74 mg/L, 17 mg/L, 18.98 mg/L and 0.64 mg/L, respectively, and the average variation coefficients were 172.92%, 141.56%, 149.87% and 34.66%, showing strong variability from May to July. During the same period, the average values of soil nitrate nitrogen in the three profile layers were 3.27 mg/L,

Table 1 Evaluation of nitrate in groundwater

Index item	Sample number	Class Ⅲ standard value (mg/L)	Exceeding standard points	Exceeding standard rate (%)	Maximum concentration (mg/L)
May nitrate (calculated as nitrogen)	20	20	13	65.00	87.97
June nitrate (calculated as nitrogen)	20	20	13	65.00	96.46
July nitrate (calculated as nitrogen)	20	20	12	60.00	75.63
August nitrate (calculated as nitrogen)	20	20	13	65.00	96.59
(May-August) Nitrate (calculated as nitrogen)	80	20	51	63.75	96.59

Table 2 Statistics of groundwater nitrate parameters (mg/L)

Project	Stage	Average value	Standard deviation	Minimum value	Maximum value	Coefficient of variation (%)
Nitrate in groundwater	May	35.98	25.11	0.61	87.97	69.80
Nitrate in groundwater	June	33.72	28.32	4.68	96.46	83.98
Nitrate in groundwater	July	30.73	20.50	5.74	75.63	66.71
Nitrate in groundwater	August	38.76	27.01	10.15	96.59	69.70

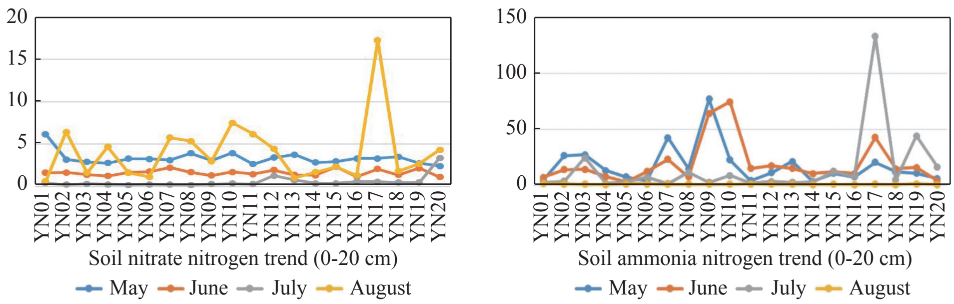


Fig. 2 Variations of nitrate nitrogen and ammonia nitrogen in surface soil

Table 3 Statistics of soil nitrogen parameter characteristics (mg/L)

Project	Stage	Average value	Standard deviation	Minimum value	Maximum value	Coefficient of variation (%)
Ammonium nitrogen (0–20 cm)	May	17.16	17.26	3.26	76.95	100.57
	June	19.12	19.12	2.99	74.36	100.01
	July	14.57	29.70	1.23	133.04	203.81
	August	0.74	0.23	0.33	1.34	31.03
Nitrate nitrogen (0–20 cm)	May	3.33	0.78	2.43	6.16	23.46
	June	1.64	0.36	1.13	2.34	22.01
	July	0.57	0.70	0.20	3.36	123.72
	August	4.04	3.74	0.60	17.21	92.68
Ammonium nitrogen (20–40 cm)	May	19.96	43.76	2.20	190.04	219.26
	June	18.31	34.62	2.25	156.32	189.12
	July	24.07	29.05	0.70	107.54	120.69
	August	0.55	0.18	0.30	0.95	32.14
Nitrate nitrogen (20–40 cm)	May	3.15	0.55	2.41	4.72	17.60
	June	1.46	0.28	1.12	2.22	19.30
	July	0.41	0.17	0.22	0.87	41.45
	August	7.85	18.60	0.59	86.11	236.91
Ammonium nitrogen (40–60 cm)	May	16.09	32.01	1.06	130.70	198.91
	June	13.58	18.41	2.01	78.82	135.54
	July	18.31	22.90	0.78	93.85	125.11
	August	0.61	0.25	0.29	1.12	40.79
Nitrate nitrogen (40–60 cm)	May	3.35	0.77	2.51	5.35	22.91
	June	1.38	0.50	0.33	3.11	36.22
	July	0.42	0.12	0.21	0.70	27.61
	August	7.64	11.78	0.77	53.02	154.23

1.49 mg/L, 0.47 mg/L and 6.51 mg/L, respectively, and the average coefficient of variation were 21.33%, 25.84%, 64.26% and 161.27%. The average and coefficient of variation of nitrate in August increased greatly, showing a moderate variability. The variation coefficients of soil ammonia nitrogen and nitrate nitrogen decreased sharply from May to July and then increased sharply in August, indicating that the study area was affected by precipitation, and its random variability was strong.

3.2 Correlation of nitrate in groundwater

(1) Correlation between NO_3^- and other chemical constituents

The mass concentration of NO_3^--N in shallow groundwater is highly positively correlated with Ca^{2+}、Mg^{2+}、Cl^-、TDS and permanent hardness, which indicates that these chemical species are influencing the content of NO_3^- in the groundwater. However, they have low correlations with NO_2^- and NH_4^+ in groundwater (Table 4). The res-

Table 4 NO_3^- correlation analysis with groundwater chemical factors

Correlation coefficient	NO_3^-	Ca^{2+}	Mg^{2+}	Cl^-	TDS	Permanent hardness	NO^{2-}	NH_4^+
NO_3^-	1.00	0.85	0.72	0.73	0.89	0.94	0.05	−0.01
Ca^{2+}	0.85	1.00	0.56	0.88	0.94	0.94	0.06	0.04
Mg^{2+}	0.72	0.56	1.00	0.48	0.74	0.73	0.11	0.01
Cl^-	0.73	0.88	0.48	1.00	0.84	0.84	0.08	0.04
TDS	0.89	0.94	0.74	0.84	1.00	0.96	0.09	0.04
Permanent hardness	0.94	0.94	0.73	0.84	0.96	1.00	0.07	0.03
NO^{2-}	0.05	0.06	0.11	0.08	0.09	0.07	1.00	0.89
NH_4^+	−0.01	0.04	0.01	0.04	0.04	0.03	0.89	1.00

earch by Han et al. (2018) shows that the optimal pH range of nitrification is 6.40–7.90. The groundwater pHs in the study area fall in the range of 6.91–8.31, with an average value of 7.53. Combined with the test and analysis results, groundwater nitrification is dominant, and the mass concentration period of NO_3^--N is very high, NH_4^+-N and NO_2^--N is low.

(2) Analysis of nitrate nitrogen in groundwater and soil

From May to August, the contents of groundwater and soil nitrate increased and decreased obviously, respectively, with high consistency in time and space.

Through the cross regression fitting analysis of groundwater nitrate and soil nitrate and ammonium at different times, the goodness-of-fit coefficients of groundwater nitrate and soil nitrate in July, groundwater nitrate and soil ammonium in August, groundwater nitrate and soil nitrate in July are all greater than 0.5, and the significance is close to 0, showing a high correlation (Table 5). Through the interactive comparative analysis of data in different time periods, it is considered that the correlation between nitrate in groundwater and nitrate in soil has a certain delay.

3.3 Spatial distribution of nitrate in groundwater and soil

(1) Analysis of geostatistical characteristics

The establishment of semivariogram in geostatistics can be performed, based on the intrinsic hypothesis or the second-order stationary hypothesis, which requires that the observed values of sample points must conform to normal distribution or approximate normal distribution (Liu et al. 2021; Erik et al. 2017). The skewness coefficient of data with normal distribution is close to 0 and kurtosis coefficient should be reduced to the greatest extent. Some groundwater and soil sample data do not conform to normal distribution, but are close to normal distribution after conversion. Different semi-variogram models are selected to fit the data. The best fitting model for groundwater nitrate and soil nitrogen data from May to August and the summary of related parameters are listed in Table 6. Due to the paper space, only the spherical function range parameter fitting diagram of groundwater geostatistical model in July is shown in this paper (Fig. 3).

The best fitting models for nitrate in groundwater in May, June and August are all exponential functions, only those for July are spherical functions, and the nugget coefficients are all less than 0.25. Their spatial correlation is strong, and the interval increases from May to August, which indicates that the spatial autocorrelation distance of nitrate in groundwater in the study area is longer and the spatial continuity is stronger. The best fitting models for soil nitrate and ammonium in the four months (eight samples in total) are mostly exponential functions, and only the soil nitrate in July is spherical function. The nugget coefficient shows that the spatial correlation of soil nitrate in July and ammonium in August is strong, and the spatial correlation of soil ammonium in July is moderate, while the spatial correlation of other

Table 5 Correlation analysis of nitrate nitrogen in groundwater and soil

Nitrate nitrogen in groundwater	Soil nitrogen	Optimal model	Coefficient of goodness of fit (R^2)	Significance	Significant degree
July nitrate nitrogen	July nitrate nitrogen	three times	0.669	0.008	More relevant
August nitrate nitrogen	July nitrate nitrogen	three times	0.666	0.003	More relevant
August nitrate nitrogen	August ammonia nitrogen	compound	0.793	0	More relevant

Table 6 Correlation analysis of nitrate in groundwater and soil

Project	Stage	Sample raw data		Converted data		Model name	Gold value (C0)	Base value (C0+C)	Nugget Coefficient (C0/C0+C)	Variable a/m
		skewness	kurtosis	skewness	kurtosis					
Nitrate nitrogen in groundwater	May	0.423 2	2.116 9	0.423 2	2.116 9	Stable function	66.328 6	1 444.130 6	0.045 9	23 586
	June	1.030 6	3.794 4	−0.581 2	2.845 6	Index function	0.054 3	0.953 0	0.057 0	23 586
	July	0.658 1	2.454 9	−0.368 8	2.154 8	Sphere function	0.083 7	1.044 2	0.080 2	21 136
	August	0.800 6	2.392 9	0.092 0	1.736 1	Index function	0.087 3	1.162 2	0.075 1	23 586
Soil nitrate nitrogen	May	0.956 0	3.714 7	0.605 4	3.163 0	Sphere function	0.017 9	0.018 0	0.994 4	23 625
	June	1.155 3	4.439 9	0.575 9	3.742 4	Index function	0.030 8	0.030 9	0.996 8	23 625
	July	2.858 6	11.300 0	1.434 2	5.324 5	Sphere function	0.005 5	0.053 3	0.103 2	6 199
	August	3.549 7	14.975 0	0.521 5	3.684 5	Index function	0.919 2	0.919 3	0.999 9	23 625
Soil ammonium nitrogen	May	3.062 1	11.533 0	1.009 9	3.906 2	Index function	1.053 3	1.053 4	0.999 9	23 625
	June	2.733 4	10.060 0	0.946 1	3.471 5	Index function	0.789 6	0.790 6	0.998 7	23 625
	July	2.022 7	6.313 4	−0.227 8	2.338 5	Index function	1.071 2	1.865 8	0.574 1	16 997
	August	0.285 5	2.212 9	0.285 5	2.212 9	Exponential function	0.060 7	0.357 4	0.169 8	23 625

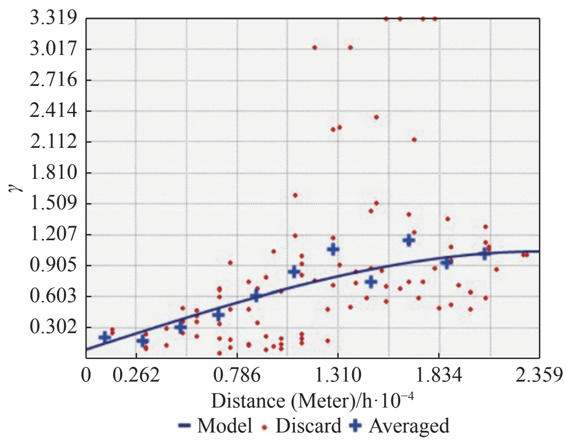


Fig. 3 Curve fitting diagram of spherical model

stages is weak. From May to August, the nugget coefficient of soil nitrogen is greater than that of groundwater. Because groundwater nitrate is affected by large-scale factors such as topography, geomorphology and climate, its random variation is small, and its spatial correlation is strong. However, soil nitrate and ammonium are affected by small-scale factors such as soil properties, precipitation, irrigation and fertilization, and their spatial structure becomes worse, and the random variability caused by human factors is enhanced, and the spatial correlation is not as strong as that of groundwater nitrate.

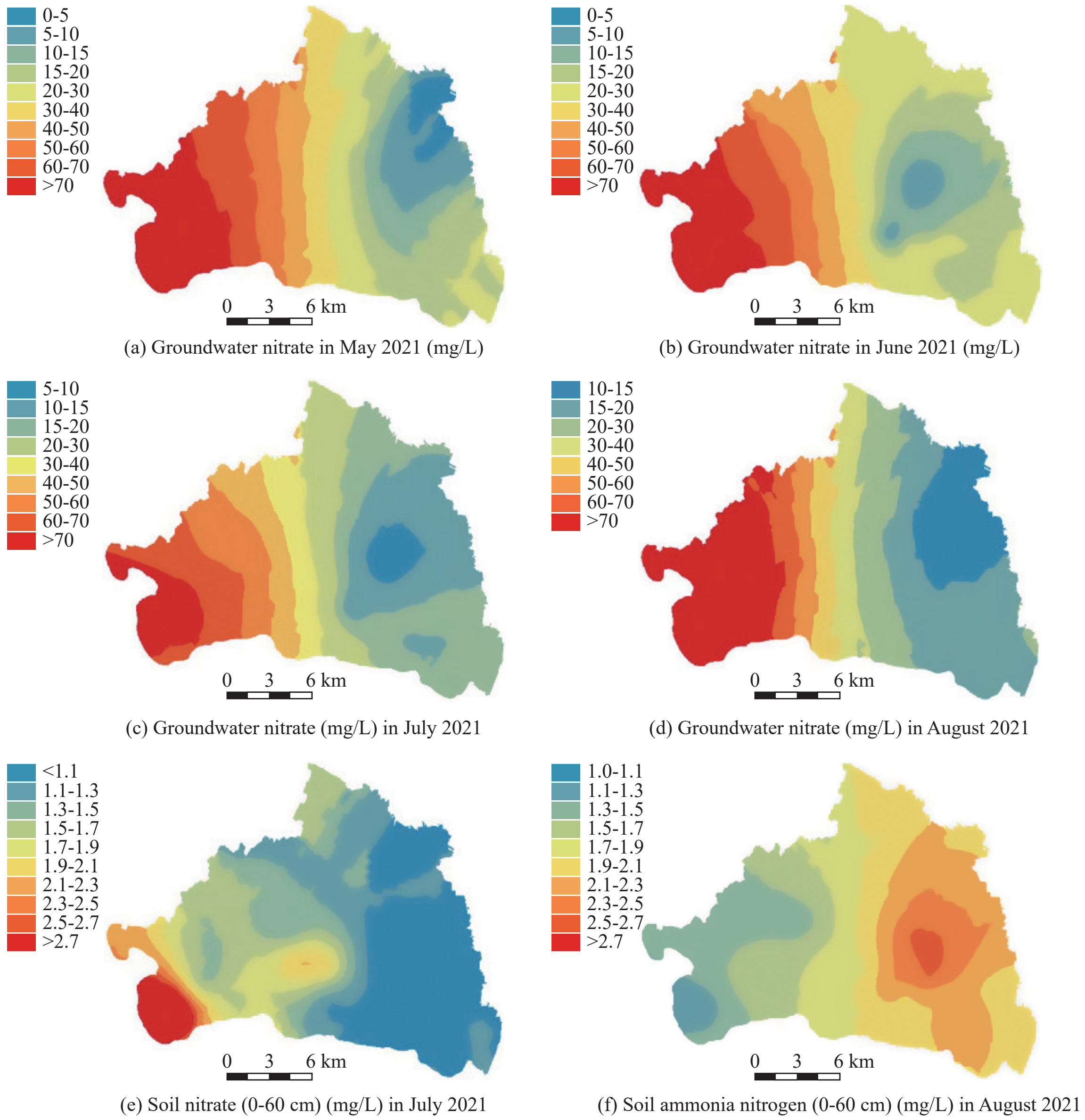
(2) Analysis of spatial distribution characteristics

Based on the statistical data, the spatial distribution trend of nitrate in groundwater is obvious and stable. The concentration of nitrate decreases linearly from north to south, and decreases in a "U" shape from west to east. The spatial distribution trends of soil nitrate and ammonia are not obvious, but the distribution changes greatly. From May to July, the soil nitrate decreases, and then in August it rises in a U-shaped trend both from north to south and from west to east. Generally speaking, ammonium contents in the south are higher than those in the other areas within the study area in May, June and August. Only in July, the ammonium in the south is lower than that in the north and the east and is higher than that in the west.

Based on analytical data of nitrate in groundwater and soil, ordinary Kriging was used for the groundwater and soil nitrate of July sampling round and soil nitrate of August sampling rounds. The nitrate spatial distributions of these sampling rounds over the study area are shown in Fig. 4. The areas with high nitrate concentration in groundwater mainly occur in the northern part of the study area, which has a high consistency with the areas of high soil nitrate content from July to August, and a high difference with the spatial position of soil ammonium content in August. In the study area, the groundwater nitrate gradually increases during the research period from May to August. The area with low-value areas of nitrate in 0–5 mg/L and 5–10 mg/L decreased from 10.97% to 0, and the area of high-value areas greater than 70 mg/L increased from 21.19% to 27.29%.

4 Conclusions

(1) Nitrate content in the groundwater in the study area became an important factor affecting the groundwater quality from May to August. Soil ammonia and nitrate contents show a moderate



(a) Groundwater nitrate in May 2021 (mg/L)
(b) Groundwater nitrate in June 2021 (mg/L)
(c) Groundwater nitrate (mg/L) in July 2021
(d) Groundwater nitrate (mg/L) in August 2021
(e) Soil nitrate (0-60 cm) (mg/L) in July 2021
(f) Soil ammonia nitrogen (0-60 cm) (mg/L) in August 2021

Fig. 4 Spatial distribution characteristics of nitrate and ammonium in groundwater and soil in different periods

variability from May to July, and the coefficient of variation decreases sharply and the increases in August, indicating that the study area was greatly affected by precipitation in August, and its random variability is strong.

(2) From May to August, the nitrate content in shallow groundwater and nitrate content in soil increase and decrease obviously at the same time. Through the quantitative analysis of cross-regression between the contents of groundwater nitrate, soil nitrate and soil ammonium for different sampling rounds, it is observed that the correlation between nitrate in groundwater and nitrate in soil is delayed for a certain period of time.

(3) From July to August, the distribution of nitrate in groundwater and nitrate in soil has a high consistency, but it is quite different from the spatial distribution of ammonium in soil in August. From May to August, the nitrate in groundwater gathers from low level to high level.

(4) There is a great correlation and delay between nitrate in groundwater and soil in the study area, which is related to many factors, such as low and concentrated precipitation, serious soil erosion, thin soil layer, the application of chemical fertilizer and the shallow water level of the Quaternary sediments.

Acknowledgements

This work was funded by Youth Fund of National Natural Science Foundation of China (42101353); And the Ministry of Housing and Urban-Rural Development Science Plan Project (2022-R-063);

Liaoning Social Science Planning Fund Project (L21BGL046). We are grateful to Shenyang Geological Survey Center of China Geological Survey for providing data support.

References

Abdelhakim L, Abdellah EH, Karima B. 2020. Spatial and statistical assessment of nitrate contamination in groundwater: Case of Sais Basin, Morocco. Journal of Groundwater Science and Engineering, 8(02): 143−157. DOI: 10.19637/j.cnki.2305-7068.2020.02.006.

Cui JS, Liu SF, Gao YK, et al. 2022. Assessment of groundwater nitrate content under land use changes in Zhanjiang City. Environmental Chemistry, 41(7): 1−12. (in Chinese) DOI: 10.7524/j.issn.0254-6108.2021071101.

Dai MX, Shi RG, Zhao YJ, et al. 2007. Spatial variability of soil cadmium in Huxian agricultural area, Sichuan Province. Journal of Agro-Environment Science, (3): 1093−1099. (in Chinese) DOI: 10.3321/j.issn:1672-2043.2007.03.058.

Han YP, Chai Y, Liu ZP, et al. 2018. Temporal and spatial distribution characteristics of nitrogen content in the groundwater of People's Victory Canal irrigation district. Journal of North China University of Water Resources and Electric Power (Natural Science Edition), 39(01): 25−30, 96. (in Chinese) DOI: 10.3969/j.issn.1002-5634.2018.

Huang S. 2019. GIS-based simulation and analysis of peak nitrate lag time in global vadose zone. Jilin University: 2019.000294. (in Chinese) DOI: 10.27162/d.cnki.gjlin.

Li JY, Li Y, Huang ZG, et al. 2022. Fertilization in intensive sugarcane planting areas significantly increased riverine nitrate pollution: Evidenced by nitrogen and oxygen isotopes in a watershed. Journal of Plant Nutrition and Fertilizers, 28(1): 104−113. (in Chinese) DOI: 10.11674/zwyf.2021513.

Li Y, Kang FX, Zou AD. 2019. Isotope analysis of nitrate pollution sources in groundwater of Dong'e geohydrological unit. Journal of Groundwater Science and Engineering, (02): 145−154. DOI: 10.19637/j.cnki.2305-7068.2019.02.005.

Liu MH, Luo SQ, Du XSH. 2021. Exploring equity in healthcare services: Spatial accessibility changes during subway expansion. ISPRS. Geo-Inf, 10: 439. DOI: 10.3390/ijgi10070439.

Ma BQ, Wang X, Tang C. 2021. Application of various environmental tracers in identifying nitrate sources of groundwater. Environmental Science and Technology, 34(06): 37−40, 44. (in Chinese) DOI: 10.19824/j.cnki.cn32-1786/x.2021.0084.

Ma CY, Wang JL, CHEN Z, et al. 2019. Spatial distribution of soil moisture estimated using thermal vegetation drought indices. Journal of Irrigation & Drainage, 38(3): 28−34. (in Chinese) DOI: 10.13522/j.cnki.ggps.20170036.

Michener R, Lajtha K. 2007. Stable isotopes in ecology and environmental science. Oxford, UK: Blackwell Publishing Ltd. https://doi.org/10.1002/9780470691854

Nixdorf E, Sun YY, Lin M, et al. 2017. Development and application of a novel method for regional assessment of groundwater contamination risk in the Songhua River Basin. Science of the Total Environment, 605-606: 598−609. DOI: 10.1016/j.scitotenv.2017.06.126.

Pati S, Dash Mihir K, Mukherjee CK, et al. 2014. Assessment of water quality using multivariate statistical techniques in the coastal region of Visakhapatnam, India. Environmental Monitoring and Assessment, 186(10): 6385−6402. DOI: 10.1007/s10661-014-3862-y.

Sacchi E, Acutis M, Bartoli M, et al. 2013. Origin and fate of nitrates in groundwater from the central Po plain: Insights from isotopic investigations. Applied Geochemistry, (34): 164−180. DOI: 10.1016/j.apgeochem.2013.03.008.

Sun XB, Cui J, Dai YJ. 2022. Research on the evaluation of land resources carrying capacity in Jinzhou area. Geological Bulletin of China, 41(08): 1487−1493. (in Chinese) DOI: 10.12097/j.issn.1671-2552.2022.08.014.

Wang YN, Xie HQ, Li FL, et al. 2020. Spatial variation analysis of intensive and economical utilization of urban land in China using ArcGIS. Geomatics & Spatial Information Technology, 43(12): 32−34, 37. (in Chinese) DOI:

10.3969/j.issn.1672-5867.2020.12.008.

Yuan HY, Yang SQ, Zhang WF, et al. 2022. Temporal and spatial variation characteristics and drivving factors of nitrogen of shallow groundwater in Hetao irrigation district. Environmental Science, 043(004): 1−15. (in Chinese) DOI：10.13227/j.hjkx.202107187.

Zhang Y, Li FD, Zhang QY, et al. 2014. Tracing nitrate pollution sources and transformation in surface-and ground-waters using environmental isotopes. Science of the Total Environment, 490: 213−222. DOI：10.1016/j.scitotenv.2014.05.004.

Zhang Z, Lu R, Wu SY, et al. 2022. Heavy metal pollution and health risk assessment of mine soil in Yangtze River economic belt. Huan Jing Ke Xue, 43(7): 3763−3772. DOI：10.13227/J.HJKX.202109102.