

Nitrate-nitrogen contamination in groundwater: Spatiotemporal variation and driving factors under cropland in Shandong Province, China

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Abstract. High groundwater nitrate-N is a serious problem especially in highly active agricultural areas. In study, the concentration and spatiotemporal distribution of groundwater nitrate-N under cropland in Shandong province were assessed by statistical and geostatistical techniques. Nitrate-N concentration reached a maximum of 184.60 mg L⁻¹ and 29.5% of samples had levels in excess of safety threshold concentration (20 mg L⁻¹). The median nitrate-N contents after rainy season were significantly higher than those before rainy season, and decreased with increasing groundwater depth. Nitrate-N under vegetable and orchard area are significantly higher than ones under grain. The kriging map shows that groundwater nitrate-N has a strong spatial variability. Many districts, such as Weifang, Linyi in Shandong province are heavily contaminated with nitrate-N. However, there are no significant trends of NO₃-N for most cities. Stepwise regression analysis showed influencing factors are different for the groundwater in different depth. But overall, vegetable yield per unit area, percentages of orchard area, per capita agricultural production, unit-area nitrogen fertilizer, livestock per unit area, percentages of irrigation areas, population per unit area and annual mean temperature are significant variables for groundwater nitrate-N variation.

1. Introduction

Natural groundwater resource provides drinking water for nearly half the population in China and other areas in world [1-3]. However, groundwater is unavoidable to be polluted by industry and municipal wastewater discharges and excessive use of fertilizer in agriculture [4, 5]. In intensive cropland areas, nitrate-N in groundwater commonly exceed natural levels, which may produce potential hazards to human health, such as birth defects, digestive cancers and leading to increase in the occurrence of an immune-system impairment [6-10].

Nitrate-N pollution in agriculture has been an environmental issue in world [11]. Higher concentrations in shallow groundwater in intensive agricultural regions are generally believed to come from agricultural activities [12]. Many efforts have been made to understand how factors affect nitrate concentration in groundwater, such as soil properties, iron, dissolved oxygen and redox conditions in groundwater and so on [13-15]. However, for mitigating nitrate pollution, it is difficult to alter these factors, such as redox conditions [16, 17]. Therefore, it is necessary to analyze the driving factors for regulating groundwater nitrate contamination. Many studies have showed that fertilizer and irrigation



in agriculture as the main factor for increasing nitrate-N concentration in groundwater [18-20]. Furthermore, manure applied in agriculture has impacted nitrate-N concentration in subsurface drainage water. Excess fertilizer in agriculture resulted in greater residual nitrate in soil and cause increased NO_3^- leaching to the groundwater [21-23]. Thus, it is imperative to grasp the correlation between agriculture and groundwater quality and develop good agricultural practices by farmers for agricultural sustainable development. Additionally, it is also necessary to understand non-artificial reasons for groundwater nitrate contamination, such as climate factors [24].

Shandong province was one of the intensive agricultural areas in the North China Plain, which called "China's granary" [25]. Monitoring and understanding trends of groundwater nitrate concentration in this area are imperative for protection of groundwater quality. Zhang W L *et al* (1996) found nitrate pollution in groundwater caused by agriculture in the North China Plain [26]. Following, many districts have been reported heavy contamination of groundwater nitrate [27-29]. Zhao T K *et al* conducted the survey of groundwater nitrate-N pollution in seven provinces of the North China, including Shandong province [30]. In recent years, many scientists carried out research from contamination evaluation, tracing source, nitrogen balance and effecting factor analysis on groundwater pollution in Shandong [29, 31-34]. However, the spatialtemporal distribution, variation trend and key factors for nitrate pollution under intensive croplands in this area are inadequate, which is conducive to develop suitable agricultural practices to alleviate the groundwater nitrate pollution. Therefore, this study aimed at protection groundwater, a strategic resource in Shandong, by analysing above problems, especially from aspects of groundwater depth, time series and comprehensive agricultural practices.

2. Materials and methods

2.1. Study area

Shandong province is located in eastern China and occupies a total area of 156,700 km². The Yellow River, running through southwest and northern part of the province, form large area of flood alluvial plain. The main crops are wheat, maize, greenhouse vegetables, cotton and orchard, and the wheat-maize rotation vegetable and fruit planting account for multitude cultivated area. The typical monsoonal climate results in 70–80% of annual precipitation concentrating from June to September in study area. The annual average temperature ranges from 11 °C to 14 °C, with greater differences in east-west region than in north-south. Annual precipitation ranges from 550 mm in the northwest to 950 mm in the southeast.

2.2. Samplings and data collection

About 2297 groundwater samples from 2006 to 2012 were collected, covering 17 cities in Shandong province (figure 1). The sampling conducted in May (before rainy season) and October (after rainy season) for every site, and mainly involved in intensive cropland, including grain, vegetable and orchard. Samples were collected in polyethylene bottles after pumping the wells for about 30 min. The pumping ensured samples not coming from the water in the storage within the wells. First, the polyethylene bottles were rinsed with the water samples to be collected to reduce the probable contamination. All samples were transported to the laboratory with an ice-cooled cabin and they were stored in a cooler until analysis. Nitrate-N concentration of water samples were analyzed in laboratory using a colorimetric method with an UV-vis spectrophotometer [35].

During sampling, basic information about well location, groundwater depth, planting pattern and surrounding land-use were collected. According to depth, sampling wells were divided into three types, shallow (0-30 m), middle-deep (30-100 m) and deep (>100 m). Furthermore, fourteen possible variables, including livestock per unit area, annual precipitation, annual mean temperature, population per unit area, percentages of crop area, percentages of grain crop area, grain yield per unit area, percentages of vegetable area, vegetable yield per unit area, percentages of orchard area, fruit yield per unit area, per capita agricultural production, percentages of irrigation areas, nitrogen fertilizer per unit

area, were assembled at the municipal level from statistical data and literatures [36, 37].

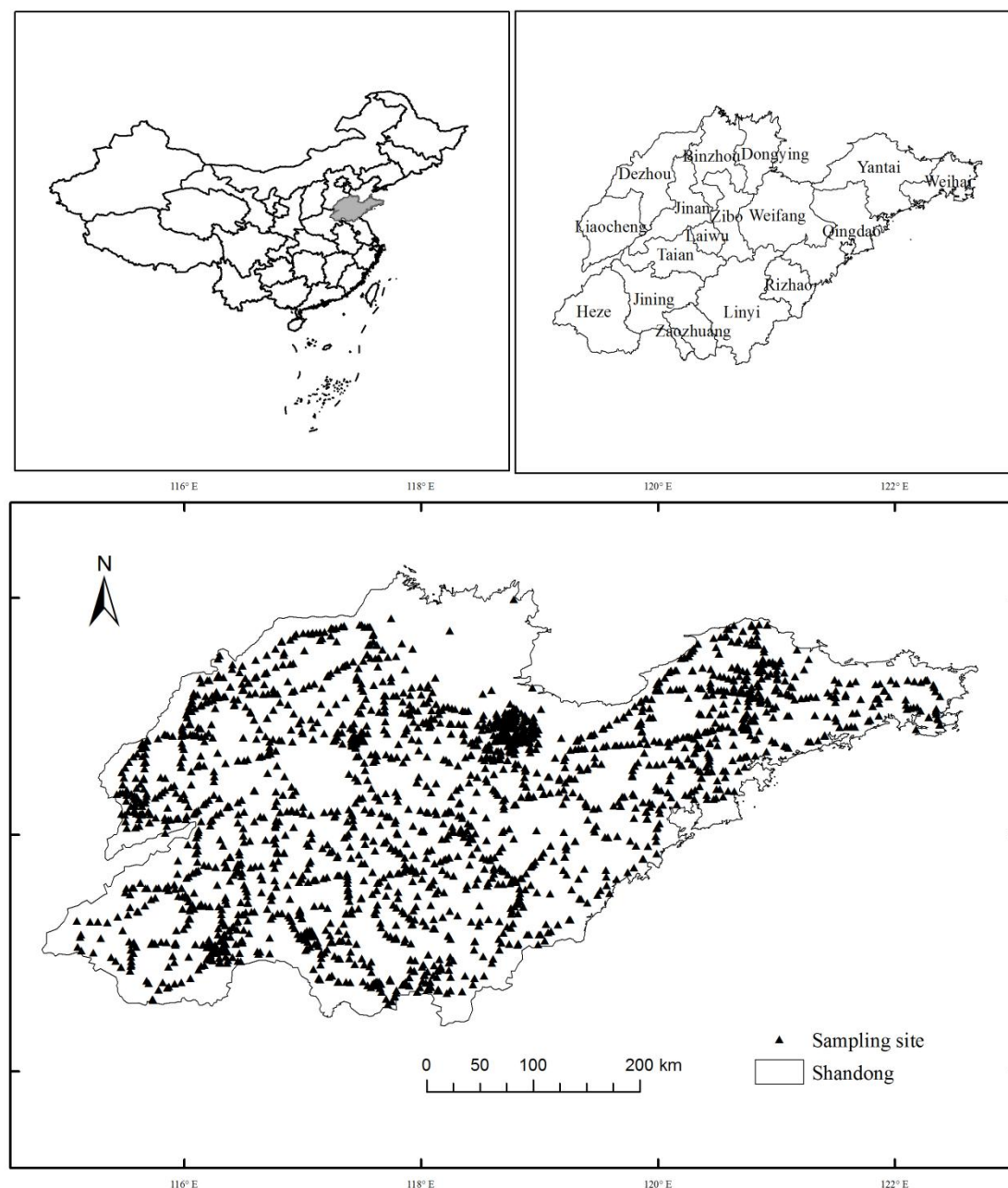


Figure 1. Sampling sites for groundwater nitrate contamination in Shandong, China from 2006 to 2012.

2.3. Statistical and geostatistical analyses

Analyzed with the Shapiro–Wilk test, the data regarding $\text{NO}_3\text{-N}$ concentration were not normally distributed. Then, the nonparametric Mann–Whitney U test or Kruskal–Wallis test were used to compare differences of groundwater nitrate–N concentration among depth, sampling seasons (before and after a rainy season) and cropland uses.

The significant factors and the regression model for nitrate–N variation were then completed by stepwise regression with stepwise Akaike’s Information Criterion (AIC). In statistical analysis,

square-root transformation was applied to all data to transform non-normal data to a data set that is reasonably normal. All statistical analyses were conducted using R software (version 3.0.3).

3. Results and analysis

3.1. Nitrate-N content in groundwater

Nitrate-N concentration collected in May from 2006 to 2012 run up to 181.60 mg L^{-1} with a median value of 9.47 mg L^{-1} , except for some sites being not detected. Correspondingly, nitrate-N concentrations in October peak at 184.60 mg L^{-1} with a median value of 10.96 mg L^{-1} , higher than those in May. According to Quality standard for groundwater in China (GB/T 14848-1993) [38], $\text{NO}_3\text{-N}$ contents in 70.56% of samples in May are below safety threshold concentration (20 mg L^{-1}), while 70.44% within the threshold in October (figure 2). In sum, there were statistically significant differences before and after rainy season (May and October, respectively) with the Mann-Whitney U test ($p < 0.05$).

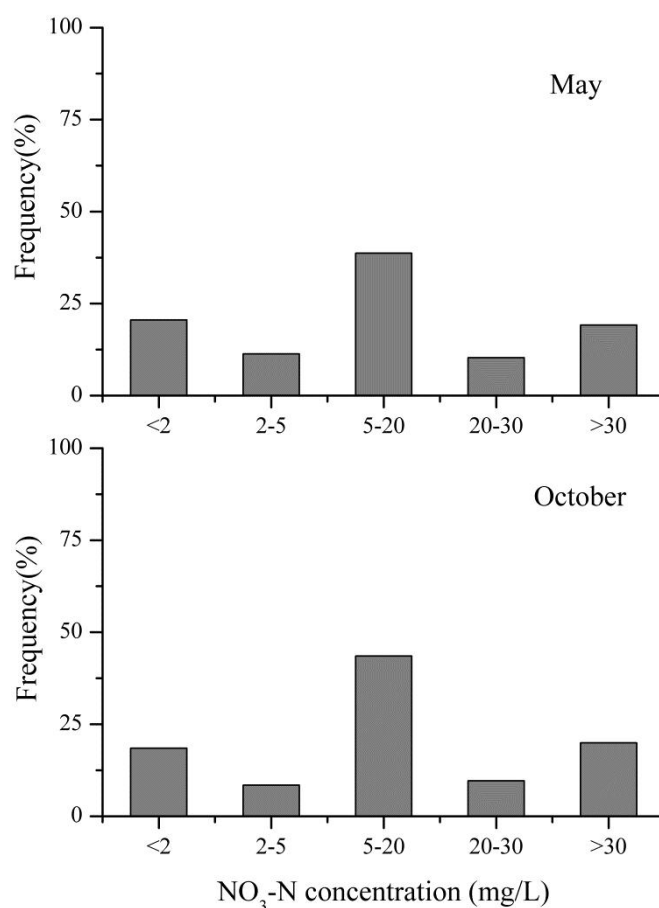


Figure 2. Frequency distribution for nitrate-N concentration in groundwater samples in May and October.

Generally, $\text{NO}_3\text{-N}$ content decreased with groundwater depth (figure 3). In study, groundwater $\text{NO}_3\text{-N}$ content in shallow wells (range= $0\text{-}184.6 \text{ mg L}^{-1}$, mean= 19.2 mg L^{-1}) are significantly higher than ones in middle-deep (range= $0\text{-}171.4 \text{ mg L}^{-1}$, mean= 16.18 mg L^{-1}) and deep wells (range= $0\text{-}181.6 \text{ mg L}^{-1}$, mean= 15.66 mg L^{-1}), analyzed with Kruskal-Wallis test ($p < 0.05$). However, there are no difference between middle-deep and deep wells ($p > 0.05$).

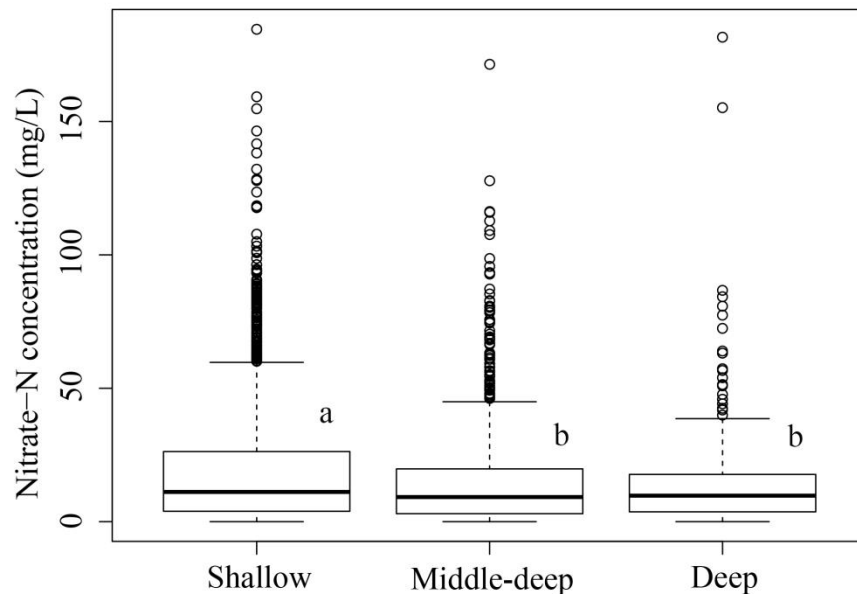


Figure 3. Comparison of measured groundwater nitrate-N concentration among three depths of wells in study area. (Different letters on each box represent a significant difference across cropland use type ($p < 0.05$)).

A non-parametric test showed there are significant differences in nitrate-N concentration among grain, vegetable and orchard with a 1% significance level (figure 4). The highest content of NO_3^- -N was under vegetable area (range=0-171.4 mg L^{-1} , mean=27.40 mg L^{-1}) followed by orchards (range=0-184.6 mg L^{-1} , mean=24.6 mg L^{-1}) and grains (range=0-155.1 mg L^{-1} , mean=13.53 mg L^{-1}). However, there are no difference between vegetable and orchard land ($p > 0.05$).

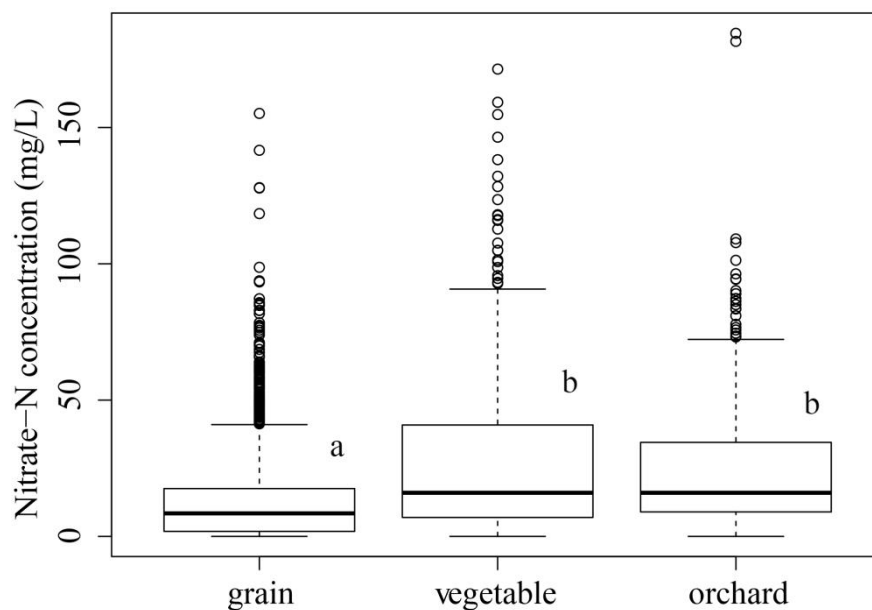


Figure 4. Comparison of measured groundwater nitrate concentration among different cropland use types in shallow wells in study area. (Different letters on each box represent a significant difference across cropland use type ($p < 0.05$)).

3.2. Spatiotemporal variability of nitrate-N

Distribution of nitrate-N contamination in study area was estimated with spatial statistics. The computed model parameters are shown in table 1. The spatial semivariogram may be affected by intrinsic (physical, chemical, and biological characteristics of hydraulic and geographic conditions) and/or extrinsic (agricultural management practices, such as fertilization, irrigation and animal wastes) factors and can be classified into three categories according to a nugget-to-sill ratio (%). A ratio of <25% indicates a strong spatial dependence, a ratio of 25%-75% indicating a moderate spatial dependence and a ratio of >75% indicating a weak spatial dependence [39]. In study, the ratios of nugget-to-sill for NO_3^- -N ranged from 0.609 to 0.742 in 2007, 2008, 2010 and 2011, showing a moderate spatial dependence, which showed NO_3^- -N might be determined by extrinsic and intrinsic factors. However, the ratios of nugget-to-sill for NO_3^- -N ranged from 0.880 to 0.999 in 2006, 2009 and 2012, indicating a weak spatial dependence and NO_3^- -N might be affected by extrinsic factors.

Table 1. Model parameters for semivariograms of logit-transformed NO_3^- -N concentration in shallow wells in Shandong from 2006 to 2012.

year	Model	Nugget	Sill	Range (m)	Nugget/Sill	r^2	RSS
2006	Exponential	0.001	1.779	43000	0.999	0.167	0.355
2007	Spherical	0.495	1.373	332000	0.639	0.949	0.0327
2008	Exponential	0.767	2.609	284000	0.706	0.921	0.138
2009	Spherical	0.192	1.596	684000	0.88	0.964	0.0466
2010	Exponential	0.222	0.86	2110000	0.742	0.817	0.0031
2011	Exponential	0.322	0.823	73000	0.609	0.671	0.04
2012	Spherical	0.229	2.042	1270000	0.888	0.93	0.0598

Spatial distribution of nitrate-N concentrations was shown in figure 5. The location and areal coverages of five NO_3^- -N concentration classes were different from 2006 to 2012. According to Quality standard for groundwater in China [38], the safety threshold interval of NO_3^- -N (< 20 mg L^{-1}) generally occupy the majority area in study, especially in 2008 and 2009. On the contrary, areas with the higher interval of NO_3^- -N (> 30 mg L^{-1}) is relatively more in 2006. Kriging prediction maps indicated that higher nitrate-N concentration mainly encountered in the middle-eastern region of Shandong, and Weifang and Linyi district have been hotspot areas for nitrate-N contamination. However, NO_3^- -N concentration of groundwater is relatively low in western area in Shandong.

Temporal variability of groundwater nitrate-N in study area, as depicted in figure 5, had a certain trend over the years. Generally, mean nitrate-N concentration decreased from 2006 to 2009, and increased from 2009 to 2013. Additionally, the mean measured nitrate-N concentrations in 17 cities of Shandong province from 2006-2012 in shallow, middle-deep and deep wells are all listed in table 2. However, the Mann-Kendall trend test showed there are no significant trends for most cities for the 7-year period ($p>0.05$), except Rizhao city. The latter had positive significant Kendall's Tau values in deep groundwater, consistent with an upward trend of nitrate-N concentrations over the 7-year period. In contrast, other cities had no significant Kendall's Tau values, probably indicating there is no clear trend in nitrate-N concentration over the years.

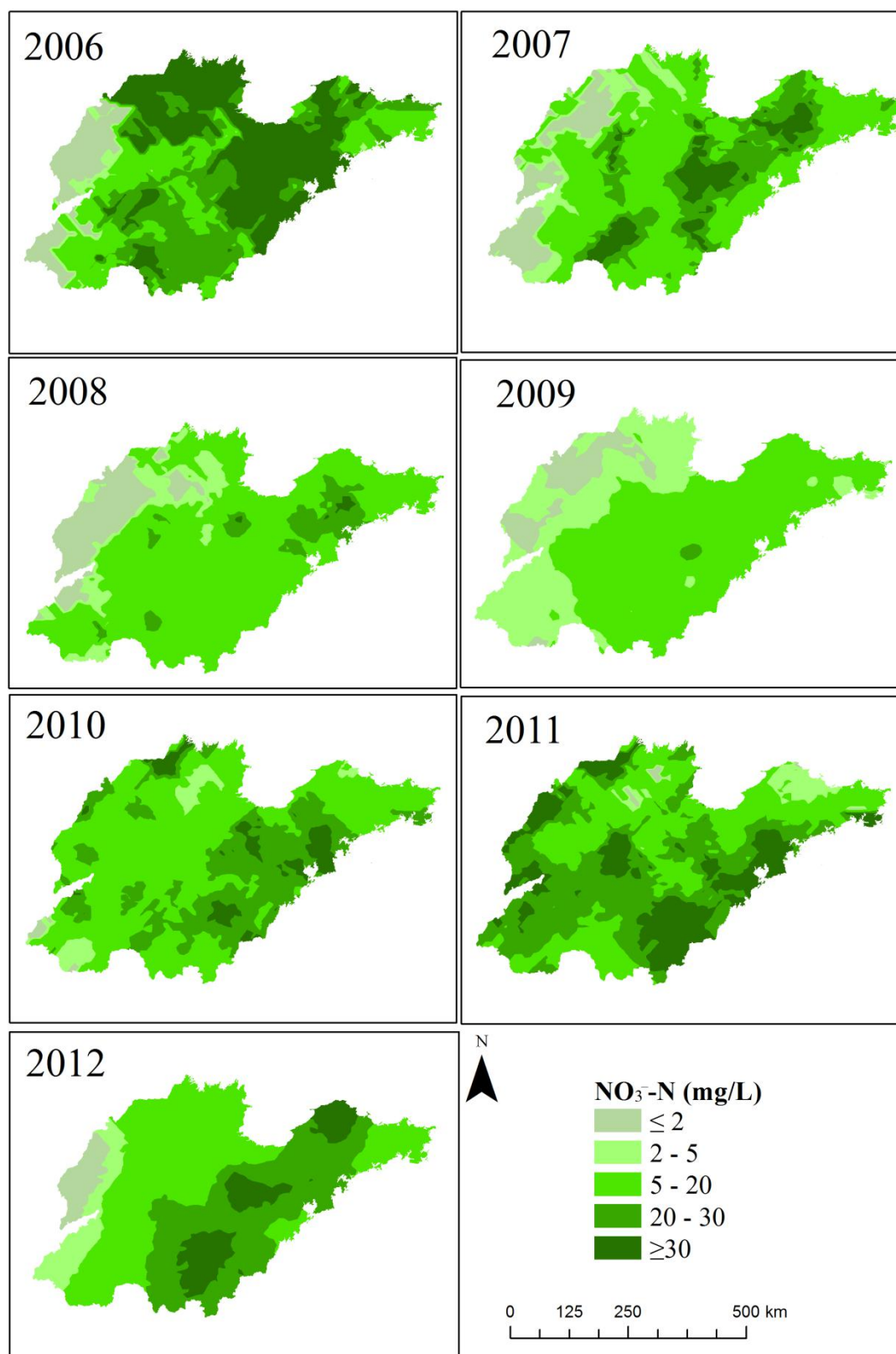


Figure 5. Spatial and spatiotemporal nitrate variability in groundwater resources of Shandong regions, China, 2006-2012.

Table 2. Mean nitrate-N (mg L⁻¹) and the Mann-Kendall trend test results for nitrate concentrations in the time series of wells during 2006-2012 in Shandong province, China.

City	well deep	NO ₃ -N concentration								Kendall's	
		2006	2007	2008	2009	2010	2011	2012	Mean	tau	p
Binzhou	1	21.17	9.38	4.42	2.11	23.35	16.22	7.04	11.96	-0.143	0.764
	2	0.17	0.56	1.14	--	6.05	0.81	8.91	2.94	0.733	0.060
	3	--	3.04	7.73	0.03	4.89	--	9.39	5.02	0.40	0.462
Dezhou	1	24.33	2.46	3.64	1.03	26.41	42.40	8.55	15.54	0.238	0.548
	2	0.56	2.68	1.05	1.74	4.58	6.70	1.64	2.71	0.429	0.230
	3	--	--	0.12	0.20	5.92	--	--	2.08	1.0	1.0
Dongying	2	--	0.18	0.46	0.00	--	--	--	0.21	-0.333	1.0
	3	--	0.00	--	1.72	3.87	--	--	1.86	1.0	1.0
Heze	1	13.35	0.61	4.64	1.95	13.93	30.12	2.36	9.56	0.238	0.548
	2	--	0.18	0.06	7.36	4.18	22.57	0.49	5.81	0.333	0.452
Jinan	1	13.72	10.74	6.08	4.92	22.56	8.35	21.75	12.59	0.048	1.000
	2	18.79	31.36	21.93	--	8.70	11.29	13.05	17.52	-0.333	0.452
	3	1.58	7.31	2.13	1.05	9.30	50.37	10.50	11.75	0.524	0.133
Jining	1	18.87	10.53	16.13	3.90	10.97	13.28	11.39	12.15	-0.143	0.764
	2	41.35	9.17	7.48	4.93	9.18	48.77	5.65	18.07	-0.143	0.764
	3	0.19	28.38	5.54	4.21	11.75	16.53	17.92	12.08	0.429	0.230
Laiwu	1	28.66	4.29	9.47	6.78	6.99	33.70	19.06	15.56	0.238	0.548
	2	9.63	8.27	8.76	--	--	--	--	8.88	-0.333	1.0
	3	--	2.08	7.11	--	--	--	--	4.60	--	--
Liaocheng	1	0.28	2.80	0.34	2.04	21.41	27.44	0.72	7.86	0.429	0.230
	2	0.85	0.74	0.30	1.86	6.30	4.95	0.42	2.20	0.143	0.764
	3	--	0.02	--	5.76	3.87	--	--	3.22	0.333	1.000
Linyi	1	20.12	21.51	10.96	10.60	25.18	37.87	32.17	22.63	0.429	0.230
	2	14.79	11.13	9.80	10.54	19.88	27.08	25.83	17.01	0.429	0.230
	3	13.60	20.67	15.81	--	18.04	--	--	17.03	0.333	0.734
Qingdao	1	61.95	26.44	23.34	8.31	29.92	35.75	23.02	29.82	-0.238	0.548
	2	45.42	14.14	21.17	6.01	31.61	36.11	25.32	25.68	0.048	1.0
Rizhao	1	--	9.86	7.13	6.57	--	--	--	7.85	1.0	1.0
	2	68.94	28.88	9.17	--	36.23	35.23	16.43	32.48	-0.333	0.452
	3	--	--	2.66	3.96	13.88	19.65	22.85	12.60	1.0	0.027
Taian	1	25.67	10.81	8.80	8.24	17.10	27.30	19.88	16.83	0.143	0.764
	2	4.72	17.29	21.91	8.02	18.27	35.55	25.88	18.81	0.619	0.072
	3	--	10.05	5.54	7.06	14.55	47.03	17.60	16.97	0.60	0.133
Weifang	1	40.29	30.28	13.84	9.53	27.69	22.27	26.46	24.34	-0.333	0.368
	2	22.83	27.43	17.74	9.22	24.58	23.88	23.80	21.35	-0.048	1.000
	3	0.83	32.94	5.12	11.20	14.18	14.71	24.49	14.78	0.524	0.133
Weihai	1	--	17.23	11.42	5.96	--	--	--	11.54	1.0	1.0
	2	--	5.59	8.35	8.73	25.37	32.02	7.53	14.60	0.467	0.260
Yantai	1	36.40	29.24	21.91	7.69	13.54	8.97	30.35	21.16	-0.333	0.368
	2	13.23	28.21	8.01	8.39	9.58	5.96	29.57	14.71	-0.048	1.000
	3	--	11.23	23.14	11.17	14.69	9.67	14.15	14.01	-0.20	0.707
Zaozhuang	1	45.65	43.31	12.48	7.91	20.66	16.93	32.28	25.60	-0.238	0.548
	2	21.27	21.66	20.60	6.77	3.70	1.50	24.26	14.25	-0.333	0.368
	3	--	14.56	9.85	20.04	--	--	--	14.82	0.333	1.000
Zibo	1	--	10.03	7.85	7.57	4.62	0.77	18.42	8.21	-0.333	0.452
	2	4.44	8.53	9.73	8.88	3.34	0.22	10.19	6.48	0.048	1.0
	3	6.06	77.38	1.76	3.43	0.72	--	--	17.87	-0.60	0.221

Note: 1, shallow wells; 2, middle-deep wells; 3, deep wells.

^aSignificant trends are in bold ($p=0.05$). Note that cities with positive significant values had an upward trend in

nitrate concentrations over the 7-year period while those with significant negative values had a downward trend.

3.3. Analysis for effective variables

Groundwater nitrate-N varied significantly in their spatial behaviors due to many factors. To select significant variables for nitrate-N variation in three depth groundwater, a stepwise regression method with step AIC was used. Regression results showed livestock per unit area, annual mean temperature, vegetable yield per unit area, and percentages of irrigation areas are significant variables for variance of $\text{NO}_3\text{-N}$ in shallow groundwater, and in regression equation the interception is 14.71 and coefficient are 0.665, -2.7475, 1.034 and -30.36, respectively. For variance of $\text{NO}_3\text{-N}$ in middle-deep groundwater, annual mean temperature, population per unit area, vegetable yield per unit area, percentages of orchard area, per capita agricultural production and percentages of irrigation areas are significant variables, and the interception is 25.92 and coefficient of these variables are -5.78, 2.38, 0.85, -0.86, -1.50 and -33.3, respectively. Additionally, livestock per unit area, annual mean temperature, per capita agricultural production, percentages of irrigation areas and unit-area nitrogen fertilizer are significant variables for variance of $\text{NO}_3\text{-N}$ in deep groundwater, and the interception is -5.81 and their coefficient are -0.51, 2.44, 4.54, -25.63 and -3.32, respectively.

4. Discussion

According to Quality standard for groundwater in China [38], about 29.5% of groundwater samples have been in excess of $\text{NO}_3\text{-N}$ safety threshold concentration (20 mg L^{-1}), which showed groundwater nitrate-N pollution in Shandong province cannot be ignored. Long-term studies on groundwater quality monitoring are needed, which provide scientifically needed data on relationship between groundwater quality and land use management and understand if agriculture practices are effective in protecting groundwater resources.

Difference of $\text{NO}_3\text{-N}$ concentration before and after the rainy season in study is consistent with many reports, which showed larger amounts of precipitation can cause rapid infiltration ($3.8\text{--}5.8 \text{ mm/min}$). The contamination or excess fertilizer application might have entered the groundwater via heavy rainfall after the rainy season, especially from June to August [40].

Difference of groundwater nitrate-N contamination among cropland rooted in agriculture management practices such as cropping pattern, fertilizer input and irrigation amounts and methods [41]. Many reports showed excessive nitrate-N in groundwater is closely related to vegetation planting, for its higher loads of nitrogen [26, 30, 32, 42] with no exception in this research. Geospatial variation of nitrate-N concentration in figure 5 shows areas with high nitrate-N concentration locates in Weifang district, where vegetable cultivation area is larger as we all know. Additionally, with multivariate statistical analysis in study, the variable of vegetable yield per unit area is significant factor for variation of groundwater nitrate-N especially in shallow and middle-deep wells.

Besides vegetation variable, the percentage of orchard area also is significant variable for variation of nitrate-N in middle-deep groundwater. Zhao T K *et al* show groundwater nitrate-N concentration is higher under orchard area than in grain crop area [30], which is consistent with results in study. The variable of livestock per unit area is significant variable for variation of nitrate-N in shallow and deep groundwater. Previous reports showed animal wastes are considered as highly concentrated pollutants that may reach the water table [43, 44]. For sites with similar aquifer features and groundwater depth, contamination must exist in some sites located closely to a septic tank [45]. Pasten-Zapata *et al* also showed that livestock activities in a 1000-m radius contributed significantly to $\text{NO}_3\text{-N}$ in shallow groundwater in Mexico [46].

Gu *et al* reported that nitrate leakage to groundwater was significantly related to population density in 2013 [47]. The variable is significant variable for variation of groundwater nitrate-N in deep wells. The effects of natural factors (mean annual temperature and precipitation) on groundwater nitrate-N variation were different in many reports [45, 47]. In this study, variables of annual mean temperature will significantly affect nitrate-N content in three types of depth groundwater. However, precipitation is not significant variable for variation of $\text{NO}_3\text{-N}$ in study, probably for their no significant difference

among regions.

It is noteworthy that nitrogen fertilizer per unit area is only included in regression equation for nitrate-N in deep wells. Hu *et al* reported groundwater pollution by NO_3^- -N leaching occurred due to irrigation with wastewater and excessive application of fertilizers in 2005 [48]. Especially in shallow groundwater systems, frequent and excessive use of fertilizers resulted in a significant nitrate pollution [49]. During the last two decades, groundwater contaminations from extensive fertilizer applications have been reported by many studies [48-52]. Nevertheless, in this study, variables about nitrogen fertilizer and crop areas were based on unit area, and excess fertilizer in agriculture activities is normal in Shandong [53], which probably provides the reasons for having no significant difference among districts.

It has been found that unreasonable management of water and N led to nitrate pollution in groundwater and surface water [54]. Deficit irrigation has been proposed as an alternative to reduce nitrate leaching. However, agriculture in Shandong located in zones of high water demand, and flood irrigation is the common way, which is the reason that the variable of percentages of irrigation area is significant factor for variation of groundwater nitrate-N. In all, statistical analysis showed there are many influencing factors for nitrate-N variation in space and time. Perhaps, this is the reason why there is no significant trend for NO_3^- -N for many cities in Shandong.

5. Conclusions

High NO_3^- -N in groundwater is a serious problem especially in highly active agricultural areas, worldwide. In this work, nitrate-N concentration in groundwater amounts to 184.60 mg L^{-1} , and 29.5% of samples had levels in excess of nitrate-N safety threshold concentration (20 mg L^{-1}), which could result in a large risk to the health of rural populations. The median nitrate-N concentrations in October (after rainy season) were significantly higher than those in May (before rainy season). Nitrate-N content decreased with increasing groundwater depth ($p < 0.05$). And nitrate-N under vegetable and orchard area are significantly higher than ones under grain ($p < 0.05$). The kriging map of groundwater nitrate-N shows that groundwater nitrate-N has a strong spatial-temporal variability. Higher nitrate-N concentration mainly encountered in the middle-eastern region of Shandong, and Weifang and Linyi district have been hotspot areas. Generally, mean nitrate-N concentration decreased from 2006 to 2009, and increased from 2009 to 2013. Nevertheless, there are no significant trends for most cities for the 7-year period with results of the Mann-Kendall trend test.

The significant factors and the regression model for nitrate-N variation were then completed by stepwise regression, which showed livestock per unit area, annual mean temperature, vegetable yield per unit area, and percentages of irrigation areas in shallow wells, annual mean temperature, population per unit area, vegetable yield per unit area, percentages of orchard area, per capita agricultural production and percentages of irrigation areas in middle wells and livestock per unit area, annual mean temperature, per capita agricultural production, percentages of irrigation areas and unit-area nitrogen fertilizer in deep wells are significant variables for variance of NO_3^- -N.

Nitrate contamination in groundwater should be attached importance for developing and implementing strategies especially in rural areas. Measures must be taken to alleviate nitrogen pollution, such as changing the cropping pattern, adjusting the irrigation and fertilization programs and applying limited water and nitrogen fertilizers split application and reducing pollution from livestock and wastewater discharge. Results in present study may be more applicable in regions with similar climate, topography, agriculture model and urbanization in China.

Acknowledgments

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