Postprint: Seasonal Variation and Spatial Distribution Characteristics of Well Water Quality in a Typical Subtropical Agricultural Small Watershed

Authors: Luo Qiao, Li Yong, Wu Jinshui

Date: 2017-11-07T00:00:00+00:00

Abstract

Well water serves as the drinking water source for farmers in subtropical agricultural regions, and its quality directly affects the health of local farmers. This study examined ammonium nitrogen (NH4+-N), nitrate nitrogen (NO3 -N), total nitrogen (TN), and total phosphorus (TP) in well water from a typical subtropical agricultural small watershed, using geostatistical methods to analyze their seasonal variations and spatial distribution characteristics. The results indicated that the average concentrations of NH4+-N, NO3 -N, TN, and TP in well water from rural households in the study area across the four seasons were 0.05~0.10 mg(N) · L 1, 3.0~4.9 mg(N) · L 1, 3.4~5.1 mg(N) · L 1, and 0.03~0.17 mg(P) · L 1, respectively, with exceedance rates of 2.3%, 10.4%, 9.5%, and 7.9%, respectively. Regarding seasonal dynamics, NH4+-N showed no significant variation throughout the year ($P>0.05$), which was primarily related to soil adsorption; whereas NO3 -N, TN, and TP all reached their maximum values in summer and minimum values in spring, with significant differences between these two seasons ($P<0.05$), which was primarily related to agricultural fertilization activities and precipitation conditions. In terms of spatial variability, the nugget-to-sill ratio for NH4+-N, NO3 -N, TN, and TP concentrations was 0 in all seasons, and the range of each variable differed across seasons, indicating that these four variables exhibited strong spatial autocorrelation within different scale ranges in each season. Spatially, NH4+-N, NO3 -N, TN, and TP concentrations all displayed patchy distributions, with patches differing in location, size, and shape. The spatial distribution of NO3 -N and TN throughout the year was related to the topography and land use patterns of the study area, with higher concentrations in the low-lying rice cultivation areas in the southeast and southwest, and lower concentrations in the higher-elevation forest land in the north. The spatial variation coefficients of NH4+-N and TP were higher than those of NO3 -N and TN, primarily because NH4+-N is readily adsorbed by soil, while phosphorus is readily fixed in soil and difficult to migrate, resulting in relatively large differences in NH4+-N and TP concentrations across different locations. Topography, hydroclimatic conditions, soil types, land use patterns, and agricultural fertilization are the main factors causing differences in seasonal dynamics and spatial distribution patterns of well water quality in subtropical agricultural regions.

Full Text

Seasonal Dynamics and Spatial Distribution of Well Water Quality in a Small Typical Agricultural Catchment in Subtropical China

LUO Qiao[1],[2],[3], LI Yong[1],[3], WU Jinshui[1],[3]

[1]Key Laboratory of Agro-Ecological Processes in Subtropical Regions, Institute of Subtropical Agriculture, Chinese Academy of Sciences, Changsha 410125, China
[2]University of Chinese Academy of Sciences, Beijing 100049, China
[3]Changsha Research Station for Agricultural & Environmental Monitoring, Chinese Academy of Sciences, Changsha 410125, China

Abstract

Well water is the primary source of drinking water for rural populations in subtropical agricultural regions of China, and its quality directly impacts public health. This study investigated the seasonal variations and spatial distribution characteristics of ammonium nitrogen (NH_4^+-N), nitrate nitrogen (NO_3^--N), total nitrogen (TN), and total phosphorus (TP) concentrations in domestic well water within a typical agricultural catchment in subtropical China using geostatistical methods. Results showed that the average concentrations of NH_4^+-N, NO_3^--N, TN, and TP across the four seasons ranged from 0.05-0.10 $mg(N)\cdot L^{-1}$, 3.0-4.9 $mg(N)\cdot L^{-1}$, 3.4-5.1 $mg(N)\cdot L^{-1}$, and 0.03-0.17 $mg(P)\cdot L^{-1}$, respectively. The exceedance rates relative to national standards were 2.3%, 10.4%, 9.5%, and 7.9%, respectively. Seasonally, NH_4^+-N concentrations showed no significant variation throughout the year ($P > 0.05$), primarily due to soil adsorption. In contrast, NO_3^--N, TN, and TP concentrations peaked in summer and reached their lowest levels in spring, with significant differences between these two seasons ($P < 0.05$), mainly attributed to agricultural fertilization activities and precipitation patterns. Spatially, the nugget-to-sill ratios for all four variables were 0 across seasons, with each variable exhibiting different ranges in different seasons, indicating strong spatial autocorrelation at varying scales. The spatial distributions of NH_4^+-N, NO_3^--N, TN, and TP all displayed patchy patterns, though the locations, sizes, and shapes of these patches varied. The spatial distribution of NO_3^--N and TN throughout the year was associated with topography and land use patterns, with higher concentrations in low-elevation rice cultivation areas in the southeast and southwest, and lower concentrations in higher-elevation forested areas in the north. The spatial coefficients of variation for NH_4^+-N and TP were higher than those for NO_3^--N and TN, primarily because NH_4^+-N is readily adsorbed by soil while phosphorus is easily immobilized in soil, making their migration difficult and resulting in greater spatial heterogeneity. Topography, hydroclimatic conditions, soil types, land use patterns, and agricultural fertilization represent the main factors driving seasonal dynamics and spatial distribution differences in well water quality in subtropical agricultural regions.

Keywords: Subtropical zone; Rural area; Well water; Water quality; Nitrogen; Phosphorus; Land use; Geostatistics

Introduction

Groundwater pollution has become a critical environmental issue worldwide, affecting socioeconomic development and threatening daily life and human health. The World Health Organization stipulates that nitrate-nitrogen concentrations in drinking water should not exceed 10 $mg(N) \cdot L^{-1}$. When nitrate-nitrogen concentrations exceed this threshold, infants may develop methemoglobinemia, characterized by blue mucous membranes and digestive and respiratory disorders. Nitrosamines formed during nitrate transformation exhibit carcinogenic, teratogenic, and mutagenic effects. Ammonium nitrogen not only affects water odor and color, causing sensory water quality parameters to exceed standards, but can also transform into nitrite and nitrate under certain conditions, posing health risks. Excessive phosphorus in drinking water reduces calcium and vitamin D absorption in humans, particularly affecting the health of elderly populations. Over 95% of China' s rural population directly consumes groundwater, making research on nitrogen and phosphorus content in rural drinking well water particularly important.

Since the 1960s, research on agricultural non-point source water pollution has primarily focused on identifying nitrogen and phosphorus pollution sources in groundwater, influencing factors, removal technologies, and pollutant migration and transformation patterns in farmland areas. However, few studies have examined the spatiotemporal variability of nitrogen and phosphorus concentrations in rural groundwater at the watershed scale, overlooking the temporal and spatial distribution characteristics of groundwater pollution. Numerous scholars have conducted extensive research on groundwater nitrogen and phosphorus pollution. Clague et al. used $\delta^{15}N$ and $\delta^{18}O$ isotopic signatures of NO_3^- to identify nitrate sources in groundwater. Schilling et al. observed that converting land use from grassland to cropland in the Cedar River floodplain increased groundwater NO_3^--N concentrations from 0.5 $mg(N) \cdot L^{-1}$ to 25 $mg(N) \cdot L^{-1}$, with maximum values reaching 70 $mg(N) \cdot L^{-1}$. Wang et al. investigated nitrate removal using corncob as a substrate. Assegid et al. predicted water-soluble phosphorus concentrations in groundwater using geographically weighted multiple regression analysis based on groundwater level fluctuations. These studies and related remediation efforts have become topics of widespread concern in the international environmental community. For rural areas, excessive application of nitrogen and phosphorus fertilizers, discharge of untreated nitrogen- and phosphorus-containing wastewater, and improper irrigation with livestock wastewater can all lead to increased nitrogen and phosphorus concentrations in groundwater. Therefore, this study selected the Jinjing catchment, a typical small agricultural watershed in subtropical China, to analyze seasonal variations and spatial distribution characteristics of NH_4^+-N, NO_3^--N, TN, and TP concentrations in domestic well water, exploring the main factors influencing well water quality to provide a scientific basis for watershed environmental management.

1.1 Study Area Description

The Jinjing catchment is located approximately 50 km northeast of Changsha City, Hunan Province, serving as the upstream area of the Laodao River, a primary tributary of the Xiang River. The catchment lies within Jinjing Town, Changsha County, geographically positioned at 27°55 –28°40 N, 112°56 –113°30 E [Figure 1: see original paper], covering an area of 105 km^2. The region features a typical subtropical humid monsoon climate with an average annual precipitation of 1,200–1,500 mm, concentrated primarily from April to October. The mean annual temperature is 17.2°C, the frost-free period is 274 days, annual sunshine duration is 1,663 hours, and relative humidity is approximately 80%. Topography exhibits a north-high, south-low trend with elevations ranging from 43–460 m, representing a transitional zone from the hilly basins of central Hunan to the Dongting Lake Plain. The main water systems include the Jinjing, Tuojia, and Guanjia Rivers. Dominant soil types are red soil and paddy soil, with parent materials primarily composed of granite and slate shale weathering products. Land use is dominated by forestland and paddy fields, accounting for 65.5% and 26.6% of the area, respectively. Forestland is mainly distributed in higher-elevation hilly areas, while paddy fields are concentrated along both sides of lower-elevation river channels and within gullies in hilly regions. Forest vegetation consists primarily of artificial stands including Masson pine (*Pinus massoniana* Lamb.), Chinese fir [*Cunninghamia lanceolata* (Lamb.) Hook.], and oil tea (*Camellia oleifera* Abel.), with low coverage of native subtropical evergreen broadleaf forests. Paddy fields are mostly planted with double-cropping rice, with early rice typically transplanted at the end of April and harvested in mid-July, followed by late rice transplanted in mid-July and harvested in mid-October. Paddy fields are drained for sun-drying at the tillering stage (early rice: end of May; late rice: mid-August) and one week before harvest (early rice: early July; late rice: early October), remaining flooded at other times. Fertilizer is applied twice per rice season: base fertilizer (early rice: end of April; late rice: mid-July) and tillering stage topdressing (early rice: mid-May; late rice: early August). Base fertilizer consists of NPK compound fertilizer or urea, with nitrogen and phosphorus application rates of 112 $kg(N) \cdot hm^{-2} \cdot a^{-1}$ and 33 $kg(P) \cdot hm^{-2} \cdot a^{-1}$, respectively. Topdressing is primarily urea at 75 $kg(N) \cdot hm^{-2} \cdot a^{-1}$.

Therefore, total fertilizer application in paddy fields is approximately 374 kg(N) • hm^{-2} • a^{-1} and 66 kg(P) • hm^{-2} • a^{-1}. In recent years, numerous terraced tea plantations have replaced original Masson pine forests, with fertilizer application rates of 450 kg(N) • hm^{-2} • a^{-1} and 30 kg(P) • hm^{-2} • a^{-1}, applied as urea before tea picking (mid-March) and rapeseed cake in mid-December.

1.2 Sample Collection and Measurement Methods

Based on the catchment' s topographic and land use characteristics, sampling sites were distributed throughout the watershed, primarily selecting from frequently used domestic wells to achieve uniform spatial coverage and comprehensively reflect spatial distribution and seasonal variation characteristics of nitrogen and phosphorus concentrations in well water. Water quality monitoring site locations are shown in [Figure 1: see original paper]. Water samples were collected four times in April 2013, July 2013, November 2013, and January 2014, representing spring, summer, autumn, and winter, respectively, yielding a total of 481 water samples. Collected samples were refrigerated at 4°C and analyzed within one week. Measured indicators included ammonium nitrogen (NH_4^+-N), nitrate nitrogen (NO_3^--N), total nitrogen (TN), and total phosphorus (TP). NH_4^+-N was measured directly using a flow injection analyzer (Tecator FIA Star 5000 analyzer, Foss Tecator). TN was determined using alkaline potassium persulfate digestion followed by flow injection analysis. TP was measured using potassium persulfate digestion with molybdenum blue colorimetry and UV spectrophotometry (UV-2450, SHIMADZU).

1.3 Data Processing

Ordinary Kriging interpolation was used to analyze spatial distribution characteristics of NH_4^+-N, NO_3^--N, TN, and TP concentrations in well water. Data preprocessing was required prior to Kriging interpolation to ensure normal distribution. The first step involved outlier removal using the threshold method, which employs a threshold ($z \pm 3s$) to identify outliers, where z represents the mean of sample values and s represents the standard deviation. Sample values exceeding this threshold were considered outliers and replaced with the threshold value.

Following outlier removal, sample data were tested for normal distribution. If data did not follow a normal distribution, transformations such as logarithmic, cube root, square root, Box-Cox, or logit transformations were applied. Based on data analysis, this study employed the logit transformation method, which offers the advantage of easily linearizing data while preserving the original minimum and maximum values upon back-transformation. The logit transformation formula is as follows:

Where: z^+ is the standardized target variable ranging from 0 to 1; min(z) and max(z) are the minimum and maximum values of the sample data, respectively.

Examination of skewness and kurtosis revealed that the original data for NH_4^+-N, NO_3^--N, TN, and TP concentrations did not follow a normal distribution. After logit transformation, both skewness and kurtosis decreased significantly, with transformed data approximately following a normal distribution. Variograms were then calculated and fitted for NH_4^+-N, NO_3^--N, TN, and TP concentrations across spring, summer, autumn, and winter. Various theoretical models are available in geostatistics for fitting experimental variograms, including spherical, exponential, Gaussian, and Stein's parameterization of the Matérn model. The Stein parameterization of the Matérn model provided good fits for the semivariograms of logit-transformed NH_4^+-N, NO_3^--N, TN, and TP concentrations in well water. Nugget values for all variables were 0 across seasons, resulting in a nugget-to-sill ratio of 0, indicating strong spatial autocorrelation. The ranges varied among variables and seasons, with all variables showing spatial autocorrelation at different scales. After obtaining fitted variogram models, Kriging was applied to estimate regionalized variables at unsampled locations based on observed values from sampled points, generating spatial distribution maps of NH_4^+-N, NO_3^--N, TN, and TP concentrations across the entire study area. All geostatistical analyses were performed using R software.

1.4 Well Water Quality Evaluation Standards

This study referenced three national water quality standards: National Surface Water Standard (GB 3838—2002) Class III, National Groundwater Standard (GB/T 14848—93) Class III, and National Drinking Water Standard (GB 5749—2006). The standard values for drinking water in these standards are presented in . The National Groundwater Standard (GB/T 14848—93) and National Drinking Water Standard (GB 5749—2006) do not specify standards for TN and TP, while the National Surface Water Standard (GB 3838—2002) sets a standard value of 10 $mg(N) \cdot L^{-1}$ for NO_3^--N but 1.0 $mg(N) \cdot L^{-1}$ for TN, which is paradoxically lower than the NO_3^--N standard. Therefore, this study synthesized the requirements from all three standards and established threshold values of 0.5 $mg(N) \cdot L^{-1}$ for NH_4^+-N, 10 $mg(N) \cdot L^{-1}$ for NO_3^--N, 10 $mg(N) \cdot L^{-1}$ for TN, and 0.2 $mg(P) \cdot L^{-1}$ for TP in the shallow groundwater of the Jinjing catchment, with concentrations exceeding these thresholds considered polluted.

2.1 Seasonal Dynamics of Well Water Quality

Descriptive statistical analysis of NH_4^+-N, NO_3^--N, TN, and TP concentrations in domestic well water is presented in . NH_4^+-N concentrations showed no significant annual variation, with mean values of 0.05-0.10 $mg(N) \cdot L^{-1}$ and an exceedance rate of 2.3%. NO_3^--N concentrations peaked in July (summer) with a mean of 4.906 $mg(N) \cdot L^{-1}$, followed by January (winter) at 3.997 $mg(N) \cdot L^{-1}$, while April (spring) and November (autumn) showed no significant difference at 2.980 $mg(N) \cdot L^{-1}$ and 3.046 $mg(N) \cdot L^{-1}$, respectively. The NO_3^--N exceedance rate was 10.4%. TN concentrations also peaked in July at 5.058 $mg(N) \cdot L^{-1}$, followed by January and November at 4.701 $mg(N) \cdot L^{-1}$ and 3.926 $mg(N) \cdot$

L^{-1}, respectively, with the lowest value in April at 3.364 mg(N) · L^{-1}. The TN exceedance rate was 9.5%. TP concentrations were highest in July at 0.166 mg(P) · L^{-1}, followed by November and January at 0.126 mg(P) · L^{-1} and 0.080 mg(P) · L^{-1}, respectively, with the lowest value in April at 0.031 mg(P) · L^{-1}. The TP exceedance rate was 7.9%.

These results demonstrate that NO_3^--N, TN, and TP concentrations peaked in summer (July) and reached their lowest levels in spring (April), with significant differences between these seasons. This pattern likely relates to farming activities. Beginning at the end of April, farmers plant rice, and applied urea and compound fertilizers infiltrate into shallow groundwater with rainfall, reaching maximum concentrations in July. Xu et al. showed that groundwater NO_3^--N concentrations are related to fertilization practices. Additionally, research indicates that precipitation directly affects groundwater quality. Comparative analysis of temporal data on TN and TP concentrations and precipitation revealed close relationships. In 2013, total annual precipitation was 1,227 mm, with 542 mm falling in May and June alone. Nitrogen and phosphorus fertilizers applied to soils entered groundwater through leaching by rainwater, causing TN and TP concentrations in domestic well water to increase accordingly. In contrast, NH_4^+-N showed no significant seasonal variation, likely due to soil adsorption. Du et al. demonstrated that NH_4^+-N concentrations in soil profiles generally decrease from upper to lower layers, indicating that NH_4^+-N is readily adsorbed by surface soils and does not easily migrate through soil profiles or into groundwater, resulting in relatively stable groundwater NH_4^+-N concentrations.

2.2 Spatial Variability of Well Water Quality

Model parameters for semivariograms of logit-transformed NH_4^+-N, NO_3^--N, TN, and TP concentrations in domestic well water across seasons are presented in . The Stein parameterization of the Matérn model provided good fits for the semivariograms. Nugget values were 0 for all variables across all seasons, yielding a nugget-to-sill ratio of 0, indicating strong spatial autocorrelation for NH_4^+-N, NO_3^--N, TN, and TP in each season. The ranges varied among variables and seasons, with most falling within 1,000 m, except for NH_4^+-N in summer which had a range of 2,609 m. This demonstrates that these four variables exhibited spatial autocorrelation at different scales across seasons.

2.3 Spatial Distribution Characteristics of Well Water Quality

Spatial distribution patterns of NH_4^+-N, NO_3^--N, TN, and TP concentrations in domestic well water across the Jinjing catchment during 2013–2014 are shown in [Figure 2: see original paper]. All four variables displayed patchy distributions, with varying locations, sizes, and shapes of patches, indicating that natural and anthropogenic factors influencing pollution distribution operated with different intensities in different directions and at different scales. The spatial distributions of NH_4^+-N and TP patches appeared random throughout the year. In contrast, NO_3^--N and TN spatial distributions were associated with topography and land use patterns. NO_3^--N and TN concentrations were elevated in low-elevation areas with rice cultivation in the southeast and southwest, while concentrations were lower in higher-elevation forested areas in the north dominated by Masson pine, Chinese fir, and oil tea plantations. Lin et al. also demonstrated that land use type significantly affects groundwater NO_3^--N concentrations.

Spatial coefficients of variation (Table 2) showed that coefficients for NH_4^+-N and TP were higher than those for NO_3^--N and TN, particularly in April. This occurs because NH_4^+-N is readily adsorbed by soil and does not migrate easily, resulting in greater spatial differences. Coefficients of variation for NO_3^--N and TN were relatively stable, fluctuating around 100%. The TP coefficient of variation fell between those of NH_4^+-N and NO_3^--N/TN, reaching its minimum in January. The NO_3^--N/TN ratio (78%-97%) indicated that nitrogen in well water existed primarily as NO_3^--N, likely because NH_4^+-N migrating from surface soils is partially adsorbed by soil layers and partially oxidized by microorganisms to NO_3^--N, leaving NO_3^--N as the dominant nitrogen form in well water. TP concentrations ranged from 0.031-0.166 $mg(P) \cdot L^{-1}$. Generally, phosphorus is easily immobilized in soil and migrates with difficulty, with weaker leaching than nitrogen, resulting in relatively low TP concentrations that generally meet drinking water standards.

3 Discussion and Conclusion

Groundwater circulation is a complex process, and the generation, migration, and transformation of pollutants result from interactions among multiple factors. The spatiotemporal distribution patterns of TN and TP concentrations in domestic well water are closely linked to various physical, chemical, and biological processes, climate change, land use patterns, and hydrological conditions across different temporal and spatial locations within the study area. In humid climatic regions, such as intensively drained and grazed pastures in Tasmania, Australia, abundant precipitation and shallow groundwater tables facilitate infiltration to groundwater, leaching soil NO_3^--N and causing peak groundwater NO_3^--N concentrations during the first winter precipitation events. As precipitation continues during the rainy season, infiltrating water dilutes NO_3^--N, leading to decreased groundwater NO_3^--N concentrations. In semi-humid regions, such as rice-garlic (wheat) fields around Fuxian Lake in Yunnan and vegetable fields in the hilly areas of central Sichuan, lower precipitation and deeper groundwater tables mean only intense rainy season precipitation can reach groundwater, leaching soil NO_3^--N and resulting in higher groundwater NO_3^--N concentrations during or after the rainy season.

Agricultural fertilization represents another critical factor affecting groundwater nitrogen and phosphorus concentrations. Extensive nitrogen fertilizer application leads to declining nitrogen use efficiency, increasing the potential threat of groundwater contamination from nitrate leaching. Both synthetic nitrogen fertilizers and organic manure contain substantial nitrogen compounds that exist as NH_4^+-N in soil. Some is absorbed by plants, some is nitrified to NO_3^--N that infiltrates into aquifers, and some is adsorbed by soil and can be transformed into NO_3^--N under irrigation conditions, continuously entering groundwater.

Groundwater nitrogen and phosphorus concentrations also vary among different land use types. Zhao et al. compared NO_3^--N concentrations in groundwater under four land use types—vegetable fields, grain fields, orchards, and livestock operations—and found the highest exceedance rate (55.1%) in vegetable fields, followed by orchards (43.3%), grain fields (34.5%), and livestock operations (17.9%). Furthermore, land use spatial patterns significantly affect nitrogen migration and purification at the watershed scale. Liu et al. found that even without changing farming activities or types, altering land use patterns alone could modify TN loss in a small watershed.

This study demonstrated that in the seasonal dynamics of well water quality in subtropical agricultural catchments, NH_4^+-N showed no significant annual variation, mainly due to soil adsorption, while NO_3^--N, TN, and TP peaked in summer and reached their lowest levels in spring, primarily related to agricultural fertilization and precipitation conditions. Spatially, the distribution of NO_3^--N and TN was associated with topography and land use patterns, with higher concentrations in low-elevation rice cultivation areas in the southeast and southwest, and lower concentrations in high-elevation forested areas in the north. The spatial variability of NH_4^+-N and TP exceeded that of NO_3^--N and TN, mainly because NH_4^+-N is readily adsorbed by soil while phosphorus is easily immobilized, making their migration difficult and resulting in greater spatial differences. Overall, nitrogen in well water from subtropical agricultural catchments existed primarily as NO_3^--N, because NH_4^+-N migrating from surface soils is partially adsorbed by soil layers and partially oxidized by microorganisms to NO_3^--N, leaving NO_3^--N as the dominant nitrogen form.

References

[1] Aslan S, Cakici H. Biological denitrification of drinking water in a slow sand filter[J]. Journal of Hazardous Materials, 2007, 148(1/2): 253-258
[2] Basu A, Johnson T M. Determination of hexavalent chromium reduction using Cr stable isotopes: Isotopic fractionation factors for permeable reactive barrier materials[J]. Environmental Science & Technology, 2012, 46(10): 5353-5360
[3] Knobeloch L, Salna B, Hogan A, et al. Blue babies and nitrate-contaminated well water[J]. Environmental Health Perspectives, 2000, 108(7): 675-678
[4] Ward M H, Brender J D. Drinking water nitrate and health[M]//Nriagu J O. Encyclopedia of Environmental Health. Burlington: Elsevier, 2011: 167-178
[5] Buss S R, Herbert A W, Morgan P, et al. A review of ammonium attenuation in soil and groundwater[J]. Quarterly Journal of Engineering Geology and Hydrogeology, 2004, 37(4): 347-359

[6] Cai W J, Chang C P, Song S, et al. Spatial distribution and sources of groundwater phosphorus in Dezhou Region[J]. Chinese Journal of Eco-Agriculture, 2013, 21(4): 456-464
[7] Zhang X Y, Xin B D, Wang X H, et al. Progress in research on groundwater pollution in our country[J]. Earth and Environment, 2011, 39(3): 415-422
[8] Clague J C, Stenger R, Clough T J. Evaluation of the stable isotope signatures of nitrate to detect denitrification in a shallow groundwater system in New Zealand[J]. Agriculture, Ecosystems & Environment, 2015, 202: 188-197
[9] Schilling K E, Jacobson P J, Vogelgesang J A. Agricultural conversion of floodplain ecosystems: Implications for groundwater quality[J]. Journal of Environmental Management, 2015, 153: 74-83
[10] Wang X M, Xing L J, Qiu T L, et al. Simultaneous removal of nitrate and pentachlorophenol from simulated groundwater using a biodenitrification reactor packed with corncob[J]. Environmental Science and Pollution Research, 2013, 20(4): 2511-2518
[11] Assegid Y, Melesse A M, Naja G M. Spatial relationship of groundwater-phosphorus interaction in the Kissimmee river basin, South Florida[J]. Hydrological Processes, 2015, 29(6): 819-827
[12] He S H, Wen Z Q, Lou T. Experiment Design and Data Processing[M]. Changsha: National University of Defense Technology Press, 2002: 127-128
[13] Hengl T, Heuvelink G B M, Stein A. A generic framework for spatial prediction of soil variables based on regression-kriging[J]. Geoderma, 2004, 120(1/2): 75-93
[14] R Development Core Team. R: A language and environment for statistical computing[EB/OL]. [2015-11-26]. http://www.r-project.org/
[15] Xu C Y, Li Y Z, Li Q Z, et al. Nitrate contamination and source tracing from NO_3^--$\delta^{15}N$ in groundwater in Weifang, Shandong Province[J]. Acta Ecologica Sinica, 2011, 31(21): 6579-6587
[16] Zhang T, Chen S J, Fu J F. Analysis of three-nitrogen concentration and spatial-temporal distribution of groundwater in Sihu Region[J]. Resources and Environment in the Yangtze Basin, 2014, 23(9): 1295-1300
[17] Du Z J, Chen X M, Zhang J B, et al. Time-spatial variability of nitrate and ammonium in dry land of typical red soil under long-term fertilization[J]. Chinese Journal of Soil Science, 2010, 41(3): 611-616
[18] Lin H T, Jiang L H, Song X Z, et al. Nitrate concentration of groundwater and its affecting factors in Shandong Province, China[J]. Journal of Agro-Environment Science, 2011, 30(2): 340-347
[19] Chen X M, Wo F, Chen C, et al. Seasonal changes in the concentrations of nitrogen and phosphorus in farmland drainage and groundwater of the Taihu Lake region of China[J]. Environmental Monitoring and Assessment, 2010, 169(1/4): 159-168
[20] Addiscott T M, Thomas D. Tillage, mineralization and leaching: Phosphate[J]. Soil and Tillage Research, 2000, 53(3/4): 255-273
[21] Holz G K. Seasonal variation in groundwater levels and quality under intensively drained and grazed pastures in the Montagu catchment, NW Tasmania[J]. Agricultural Water Management, 2009, 96(2): 255-266

[22] Li Z Z, Gao H Y, Zhang Q, et al. Nitrate pollution of groundwater and the affecting factors in typical farmlands of Fuxianhu Lake Catchment[J]. Journal of Agro-Environment Science, 2008, 27(1): 286-290

[23] Chen K L, Zhu X D, Zhu B, et al. Temporal and spatial variation of NO_3^--N pollution in groundwater in small watershed of Central Sichuan Basin[J]. Journal of Agro-Environment Science, 2006, 25(4): 1060-1064

[24] Wang Q S, Gu Y, Sun D B. Spatial and seasonal variations of nitrate-N concentration in groundwater within Chao Lake watershed[J]. Acta Ecologica Sinica, 2014, 34(15): 4372-4379

[25] Zhang Y L, Zhang Y Z, Zhang Y, et al. Characteristics and potential sources of nitrate pollution in surface water and groundwater systems in Taizihe River Basin[J]. Chinese Journal of Eco-Agriculture, 2014, 22(8): 980-986

[26] Ma H B, Li X X, Hu C S. Status of nitrate nitrogen contamination of groundwater in China[J]. Chinese Journal of Soil Science, 2012, 43(6): 1532-1536

[27] Liu X Q, Xu J Y, Jiang L H, et al. Spatial variability and distribution pattern of groundwater nitrate pollution in farming regions of Shandong Province, China[J]. Journal of Agro-Environment Science, 2010, 29(6): 1172-1179

[28] Zhao T K, Zhang C J, Du L F, et al. Investigation on nitrate concentration in groundwater in seven provinces (city) surrounding the Bo-Hai Sea[J]. Journal of Agro-Environment Science, 2007, 26(2): 779-783

[29] Liu Y Y, Shi S, Mu Z J, et al. Dynamic changes of water nitrogen and phosphorus concentrations in a typical small agricultural watershed of the Three-Gorges Reservoir Region[J]. Journal of Southwest University: Natural Science Edition, 2014, 36(11): 157-163

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.