

Nitrogen contamination in groundwater in an agricultural region along the New Silk Road, northwest China: distribution and factors controlling its fate

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Abstract Nitrogen contamination is a global concern and has been a serious problem in agricultural areas. The present study was carried out in an intensively irrigated region of northwest China along the New Silk Road, Yinchuan Plain, where the residents depend on the groundwater as the primary source for drinking. To understand the nitrogen contamination in the aquifer system, the distribution of nitrate and ammonium and its controlling factors were studied based on hydrochemical, hydrogeological, and isotopic analyses. 11.37 and 40% of phreatic water samples are categorized as $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ pollution in accordance with the WHO standards. A total of 59.52% of confined water samples has high $\text{NH}_4\text{-N}$ values, exceeding the permissible limit for drinking purpose. The results indicate $\text{NO}_3\text{-N}$ predominates in the shallow water and $\text{NH}_4\text{-N}$ predominates in the deep water for the single phreatic aquifer. For the multilayer structure area, $\text{NO}_3\text{-N}$ predominates in the phreatic aquifer of the western and the southern parts of the plain; $\text{NH}_4\text{-N}$ predominates in the phreatic aquifer of the middle and the northern parts of the plain, and in the confined aquifers where groundwater pumping had been performed. The mixture of synthetic fertilizer and manure/sewage is primarily responsible for the phreatic water based on isotopic analysis. In the confined aquifers, higher $\text{NH}_4\text{-N}$ concentrations are mainly attributed to

intensive pumping under higher pumping rates. The results of this study can be used as a scientific basis for the future research on nitrogen in the plain. They can also be used by scholars and decision makers who are interested in groundwater protection and sustainable development.

Keywords Nitrate · Ammonium · Hydrogeological properties · Redox conditions · Groundwater pumping · New Silk road · China

Introduction

Groundwater is one of the most important sources of water for human due to its natural purity. The utilization of the finite groundwater resource, however, is being compromised with water of poor chemical quality, especially when it contains high level of nitrogen (N) (Heaton et al. 2012). Anthropogenic sources through agricultural activities, disposal of human and animal sewage, industrial wastes discharge, and landfill leachate, are major contributors to nitrogen contamination, resulting in adverse impacts on economy, ecosystem and human health (Böhlke et al. 2006; Umezawa et al. 2008; Yoshimoto et al. 2011; Wu and Sun 2015). For example, exposure to high level of nitrogen contamination through drinking water may lead to methemoglobinemia (blue baby syndrome) and cancer in humans (Low 1974; Ward et al. 2005; Li et al. 2014a; Marinov and Marinov 2014). Therefore, in most regions of the world, the significant increase of nitrogen in groundwater is a growing concern (Gustafson 1983; Li et al. 2006; Serhal et al. 2008; Subramani et al. 2010).

Nitrate (NO_3^-) and ammonium (NH_4^+) are the two most important forms of nitrogen. As NH_4^+ can be easily oxidized, nitrate is the most common contamination of aquifer systems

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(Umezawa et al. 2008; Welch et al. 2011). However, behavior of nitrogen in an aquifer depends heavily on multiple factors, such as nitrogen loading, biogeochemical processes, hydrogeological properties, and groundwater pumping. Land use type and fertilizer application rates largely determine the amount of nitrate in many agricultural areas (such as Diez et al. 2000; Thorburn et al. 2003; Ju et al. 2006; Kaown et al. 2009; Li et al. 2014a, 2016a). High concentrations of ammonium in shallow and deep groundwater are more often controlled by point sources and organic matter in sediment (Böhlke et al. 2006; Singh et al. 2006; Hinkle et al. 2007). Because biological cycling of nitrogen often occurs with changes in isotopic ratios, the combined use of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ in nitrate has been widely reported for identification of actual sources and related processes (such as volatilization, nitrification and denitrification) (Mayer et al. 2002; Hosono et al. 2013; Pastén -Zapata et al. 2014; Zhang et al. 2014). In addition, many studies have pointed out the significant effects of local hydrogeological conditions on nitrogen behavior. For instance, the study conducted by Han et al. (2015) demonstrated that groundwater mean residence time determined redox conditions, significantly affecting the nitrate concentrations in the shallow Quaternary aquifers. Due to the presence of an aquitard, the nitrate exhibited distinct characteristics in the aquifer of an agricultural area (Nishikiori et al. 2012). As pumping of groundwater can change the groundwater table and the characteristics of the flow system, it can also affect the fate of contamination (Li et al. 2014b, 2016a; Park et al. 2014). Dragon (2012) performed an investigation of nitrate in a regional Quaternary flow system, and found that the high concentrations of nitrate at great depth were caused by pumping. In recognition of these, before taking action to prevent groundwater contamination, it is quite important to understand the nitrogen distribution and the factors controlling its fate in aquifer system.

Yinchuan Plain is an important agricultural area in northwest China along the New Silk Road, where nearly three million population depend on groundwater for drinking. In the irrigated area, the excessive application of N fertilizer did help produce higher crop yields, but the nitrogen contents in groundwater were also elevated. Field investigations showed that the suitability of groundwater for drinking purpose was greatly affected by high nitrogen concentrations, which are above the permissible standards of World Health Organization (WHO 2011) ($\text{NO}_3\text{-NN} > 10 \text{ mg/L}$, $\text{NH}_4\text{-NN} > 0.2 \text{ mg/L}$). Furthermore, high rate of pumping over the recent decades has caused serious groundwater declines, and groundwater from the phreatic aquifer has been leaking into the confined aquifers, especially in the cone of depression areas (Qian et al. 2013; Chen et al. 2015). It is quite possible that groundwater with high nitrogen leaks into the confined aquifers, deteriorating the water quality. In this context, to build a new and

sustainable Silk Road Economic Belt, it is necessary to recognize the threats of nitrogen in the aquifer system (Li et al. 2015a). Although several studies regarding soil and groundwater pollution have been carried out in and around the plain, including Li et al. (2014b, c, 2015b, 2016b), Qian and Li (2011), Qian et al. (2012, 2013, 2014), and Wu et al. (2014, 2015a), few nitrogen investigations have been reported. There is limited knowledge on nitrogen contamination at a regional scale. The distribution of nitrogen and the factors controlling its fate in the aquifer system remain unclear. All these make it more difficult to take effective action for contamination prevention.

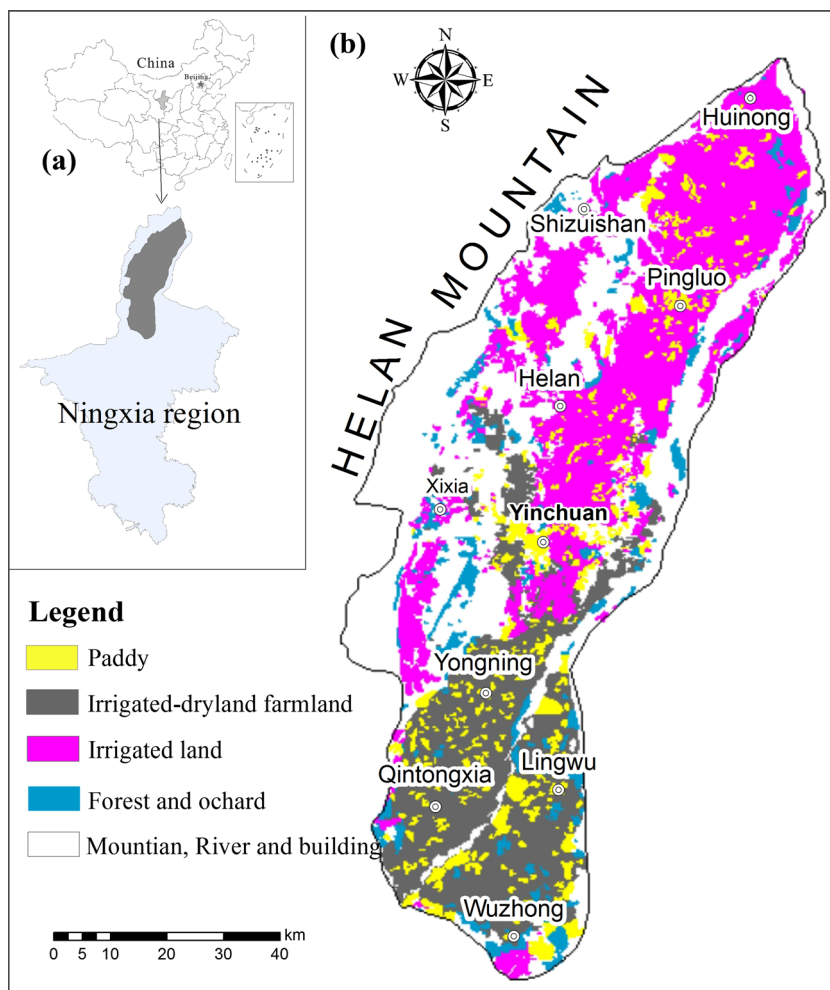
The aim of this study is to gain a better understanding of nitrogen contamination in the aquifer system. In this study, the concentrations and distributions of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in the aquifer system were investigated. Based on the evaluation of the hydrogeological conditions, the redox conditions of the aquifer were studied to provide general insight into the nitrogen distribution along the flow path. The status of nitrogen pollution under different hydrogeological conditions and pumping conditions were evaluated. The findings from this paper can be used as a scientific basis for future research on nitrogen in the plain. They are valuable to scholars and decision makers who are interested in groundwater protection and sustainable development.

Description of the study area

Yinchuan Plain is located in the northern part of Ningxia Hui Autonomous Region, northwest China, covering an area of 6704.5 km^2 . Due to the fertile soils in the Yellow River alluvial plain, this region is used extensively for agriculture (Fig. 1). The land use (types of crops) and the agricultural practices (flood irrigation and N application rate) are relatively uniform in the agricultural area. The climate in the area is characterized by intense evaporation and little precipitation. The average annual precipitation and evaporation are 186.7 and 1834.44 mm, respectively.

The Quaternary deposits are well developed in Yinchuan Plain with more than 2000 m in thickness (Qian et al. 2012). From west to east, the landforms are leaning pluvial plain, pluvial alluvial plain, and alluvial lacustrine plain, respectively (Fig. 2a). Overall, the groundwater flows in NNE direction. The pore water in loose rock mass, up to 250 m thick, is divided into two aquifer areas: (1) single phreatic aquifer zone and (2) multilayer structure area (Qian et al. 2013, 2014) (Fig. 2). The single phreatic aquifer zone is composed of mountain pluvial deposits and alluvial sands and gravel of the Yellow River mainly in the western and southern parts of the plain. The other regions covered by lacustrine and alluvial deposits all belong to the multilayer structure area (Fig. 3).

Fig. 1 Location of the study area and land use map



It includes a shallow phreatic aquifer underlain by two confined aquifers (upper confined aquifer and lower confined aquifer). The thicknesses of the three aquifers are 30–45, 40–130, and 60–125 m, respectively. These aquifers are separated by aquitards, which are normally continuous and vary between 2 and 14 m in thickness. The depth from the ground surface to the water table is more than 10 m in the leaning pluvial plain and less than 4.6 m in the alluvial lacustrine plain.

The water balance study between July 1, 2003, and June 30, 2004 is presented in Table 1 (Qian et al. 2012). The results show that the primary sources of recharge are from channels and irrigation infiltration. An extensive network of channels has been used to deliver water from the Yellow River for irrigation. The primary sources of discharge include evapotranspiration and artificial extraction (Table 1). Within the study area, there are thousands of pumping wells for extracting water for irrigation and drinking. In particular, the water in the confined aquifers is the primary source for municipal water supply systems that provide the drinking water for three million people living on the plain.

Groundwater chemistry is greatly affected by such factors as hydrogeological properties, chemistry of recharge water, soluble salt in soil, water–rock interactions, and evapotranspiration of phreatic water (Qian and Li 2011; Wang et al. 2013). The single phreatic aquifer zone is characterized by good permeability, high porosity, and a large hydraulic gradient. The water is mainly fresh water of $\text{HCO}_3\text{-SO}_4\text{-Ca}\cdot\text{Mg}$ and $\text{HCO}_3\text{-SO}_4\text{-Mg}\cdot\text{Ca}$ type with the total dissolved solids (TDS) generally less than 1 g/L. Variation in hydrochemical type of groundwater is observed in lacustrine and alluvial plain. In the south of Yongning, with larger hydraulic gradient and faster water cycle, the groundwater is mainly $\text{HCO}_3\text{-SO}_4\text{-Na}\cdot\text{Mg}$ and $\text{HCO}_3\text{-SO}_4\text{-Na}\cdot\text{Ca}$ type with low TDS (<1 g/L). In the north of Yongning, with smaller hydraulic gradient and the groundwater close to the ground surface, the groundwater is mainly $\text{HCO}_3\text{-Cl}\text{-Mg}\cdot\text{Na}$ type with TDS between 1 and 2 g/L and $\text{SO}_4\text{-Cl}\text{-Na}\cdot\text{Mg}$ type with TDS between 1 and 3 g/L. For some local areas, TDS can even be greater than 3 g/L partly due to intensive evapotranspiration and shallow water buried depth. Generally, groundwater

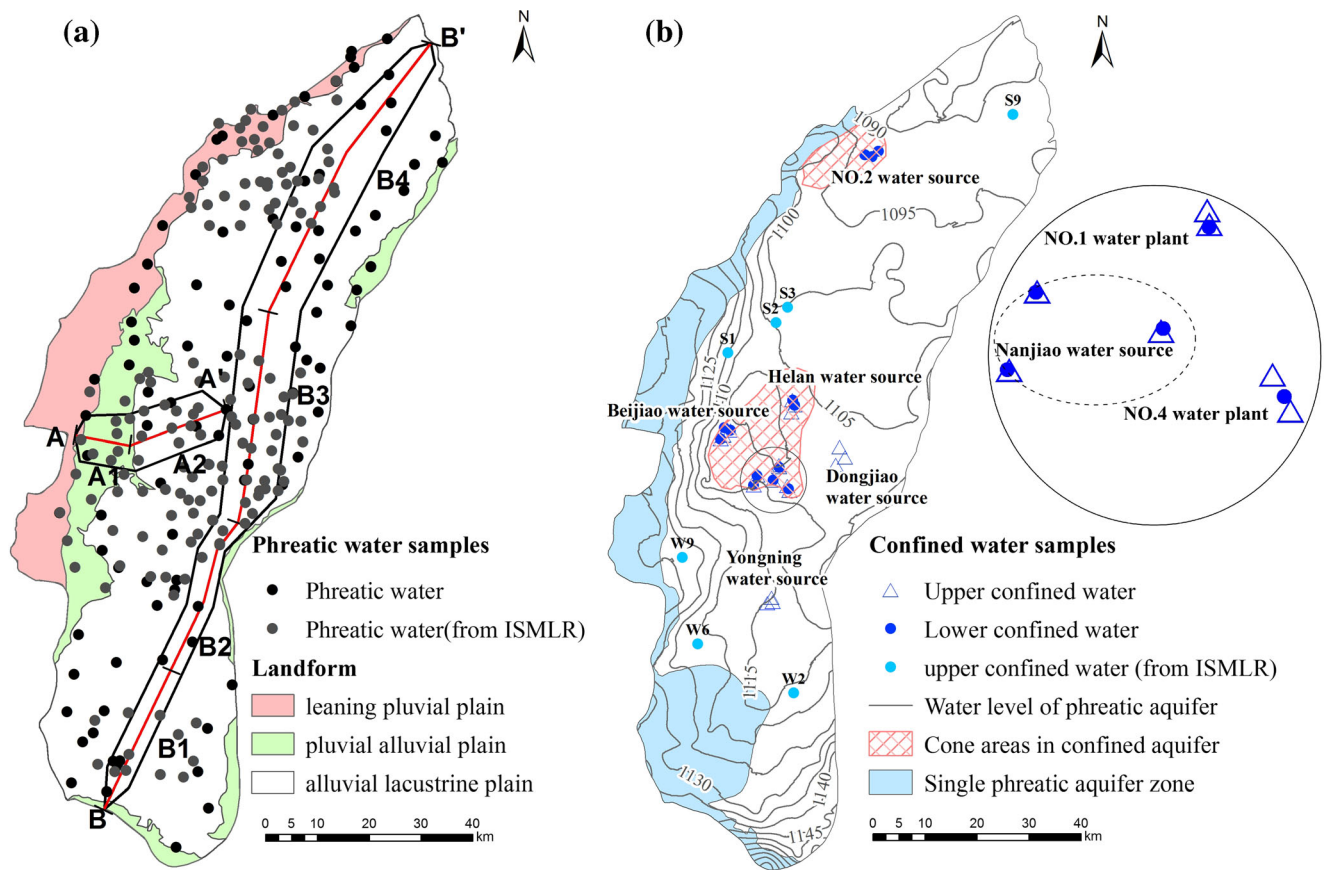


Fig. 2 A map showing landforms and sampling locations. A–A' and B–B' are two typical flow paths of phreatic water. The red lines (A–A' and B–B') also indicate the locations of the geological cross-sections presented in Fig. 3

quality becomes worse from SW to NE. Further, with the slower water circulation, the water in the confined aquifers is mainly $\text{HCO}_3\text{-SO}_4\text{-Mg}\cdot\text{Na}$ and $\text{HCO}_3\text{-SO}_4\text{-Na}\cdot\text{Mg}$ types in the south, $\text{HCO}_3\text{-Cl}\text{-Na}\cdot\text{Mg}$ type in the middle and $\text{Cl}\text{-SO}_4\text{-Na}\cdot\text{Mg}$ type in the north.

Sample collection and analyses

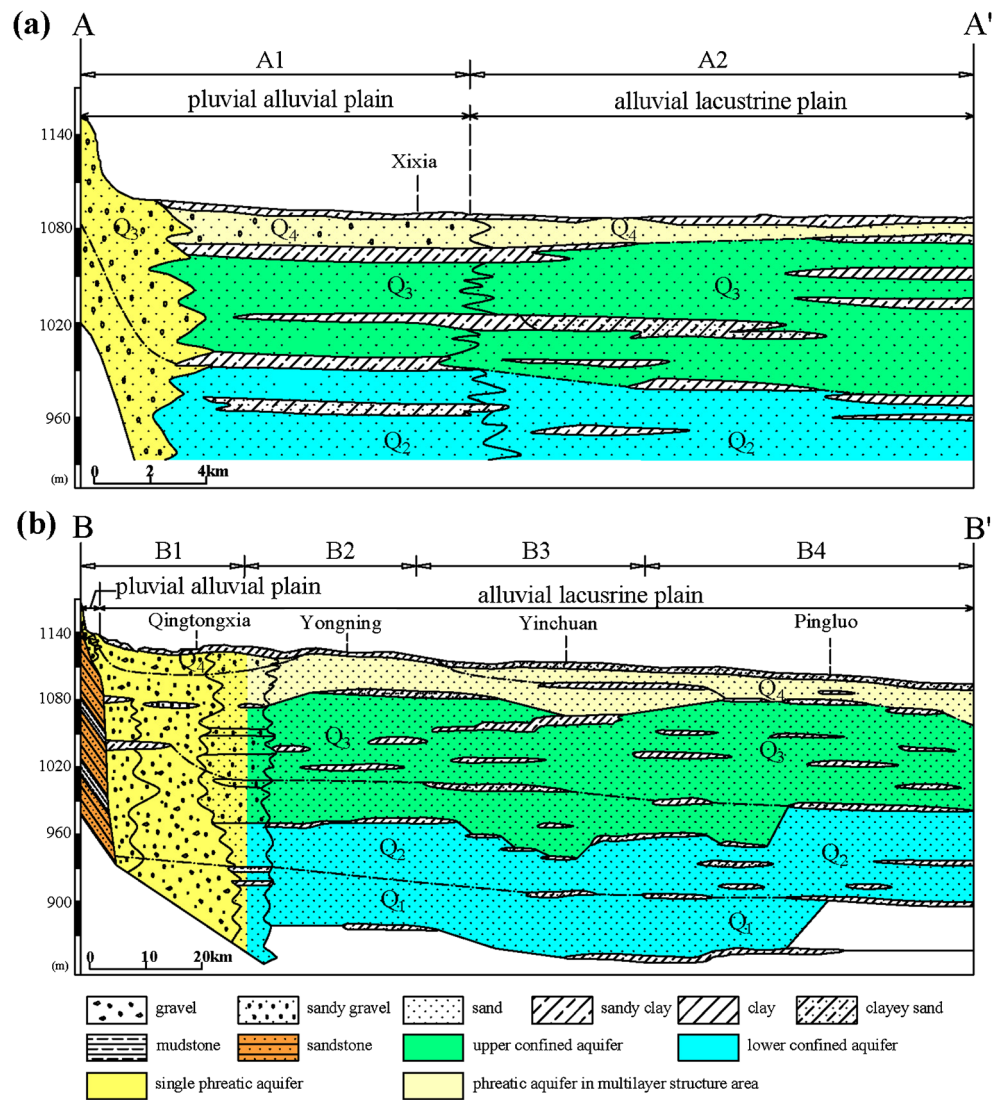
A total of 132 groundwater samples were taken from the private, irrigation, and public water supply wells in August 2013 on the study area (Fig. 2). They included 97 samples from the phreatic aquifer and 35 samples from the confined aquifers. Information on the use of the groundwater and the depth of the screen in the wells was acquired from the well managers and farmers. The sampling procedures, transportation, and conservation for all the samples followed the standard methods recommended by the Ministry of Water Resources of People’s Republic of China (PRC 1997). The water in the wells was pumped continuously for 10–15 min prior to collection of the samples. At the time of sampling, bottles were thoroughly rinsed 2–3 times with groundwater to be sampled. In addition, duplicates were introduced for

QA/QC during the analysis. $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ were analyzed using the standard methods recommended by the Ministry of Health of PRC, Standardization Administration of PRC (2006). $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ were measured by spectrophotometry and ion chromatography at laboratory of Ningxia Environmental Monitoring Center, respectively. The detection limits of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ were 0.02 and 0.025 mg/L, respectively. The analysis of ^{18}O and ^{15}N in nitrate for these samples was done by the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry Chinese academy of Science, Guizhou, China. Isotopic abundances of elements were determined using a Finnigan MAT 253 mass spectrometer and reported in the delta notation in per mill. The results of ^{18}O and ^{15}N were respectively expressed in ‰ to Vienna Standard Mean Ocean Water (VSMOW) and N_2 (air) as follows:

$$\delta(\text{‰}) = (R_{\text{sample}}/R_{\text{standard}}) \times 1000 \tag{1}$$

where R_{sample} is the isotopic ratio $^{18}\text{O}/^{16}\text{O}$ or $^{15}\text{N}/^{14}\text{N}$ of the sample, and R_{standard} is the isotopic ratio $^{18}\text{O}/^{16}\text{O}$ or $^{15}\text{N}/^{14}\text{N}$ of the standard. Analytical precisions for the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ were estimated as ± 0.2 and $\pm 0.9\text{‰}$, respectively.

Fig. 3 Cross-sections of the geological contexts and aquifer systems of A–A' (a) and B–B' (b) (see Fig. 2a for location)



Furthermore, the Institute of Survey and Monitoring of Land Resources of Ningxia (ISMLR) has carried out a large number of researches in Yinchuan Plain, and 165 samples (158 samples from the phreatic aquifer and 7 samples from the confined aquifers) were collected from private, irrigation, and monitoring wells on the plain during the same period. To provide an adequate number of data, the measured $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ values of these samples

were used in this study (Fig. 2). The sampling methods and analysis methods for these samples also followed the national standards (Ministry of Water Resources of PRC 1997; Ministry of Health of PRC, Standardization Administration of PRC 2006). Thus, the data were reliable, and the concentrations of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ from ISMLR can be used as the supplemental data to study the nitrogen contamination at a regional scale.

Table 1 Groundwater balance analyses in the Yinchuan plain from July 2003 to June 2004 (Qian et al. 2012)

Inflow	Percentage	Outflow	Percentage
Water leakage from channels	59.45%	Evaporation	46.59%
Irrigation infiltration	22.69%	Discharge from drains	21.72%
precipitation	6.54%	Discharge to Yellow River	4.27%
Boundary inflow	9.86%	Artificial extraction	27.44%
Flood recharge	1.46%		
Total Amount	$22.21 \times 10^8 \text{ m}^3/\text{a}$	Total Amount	$21.28 \times 10^8 \text{ m}^3/\text{a}$

Results and discussion

Distribution of nitrate and ammonium

Phreatic aquifer

For the samples from the phreatic aquifer, the NO₃-N concentrations range from below detection limit (BDL) to 158 mg/L with a mean level of 3.89 mg/L (Table 2). 11.37% of the samples (29 samples) exceed the acceptable limit of NO₃-N for drinking purpose (>10 mg/L) (WHO 2011). The concentrations of 111 samples are BDL. The NH₄-N concentrations vary from BDL to 31.08 mg/L with a mean level of 0.75 mg/L. It can be seen from Table 2 that 40% of them (102 samples) are not suitable for drinking without treatment due to excessive NH₄-N (>0.2 mg/L) in accordance with the WHO standard (WHO 2011). The NH₄-N concentrations BDL are found in 95 samples. Concerning the standard deviation, the most even values occurred in the phreatic aquifer for NO₃-N and NH₄-N with 12.62 and 2.93 values, respectively. Maximum values of NO₃-N and NH₄-N for all the samples (158 and 31.80 mg/L) were found in the phreatic wells, justifying the high variability.

As shown in Fig. 4 and Fig. 5, area-dependent variations of nitrogen species are observed in the phreatic aquifer. All the wells can be classified into three zones on the basis of the nitrogen species and its concentrations. (1) In the single phreatic aquifer, the vertical distribution of nitrate and ammonium concentrations is found among the samples (Fig. 5). Although no general trend between nitrogen concentration and depth of well in the phreatic aquifer, deep wells are susceptible to contamination in the zone. For the water supply wells in the southern part of the single phreatic aquifer, nitrate and ammonium contamination are still observed when the well depths are greater than 60 m. This

area is designated as Zone I where the NO₃-N and NH₄-N concentrations are rather distinct with well depths. The levels of NO₃-N are significant higher than that of NH₄-N for the shallow phreatic water in Zone I. This subpart is designated as Zone I^a. On the contrary, the species of NH₄-N is dominant and NO₃-N concentrations are BDL or very low in deep wells (>100 m). It is designated as Zone I^b. (2) In the western and the southern parts of the plain of the multilayer structure area, NO₃-N is the dominant species of nitrogen and the concentrations of NH₄-N are very low (or even BDL). This area is designated as Zone II where NO₃-N predominates in groundwater. (3) In the middle and the northern parts of the plain of the multilayer structure area, NH₄-N is the dominant species of nitrogen and the levels of NO₃-N are very low or undetectable. This area is designated as Zone III where NH₄-N predominates in groundwater.

A Mann–Whitney U test was performed to analyze the difference in NO₃-N and NH₄-N concentrations. The Mann–Whitney U test is a highly efficient nonparametric test to identify the difference between two independent samples using SPSS (version 22.0) (Miller and Miller 1988). The null hypothesis states that the two sample groups taken from a single population would have no consistent differences between the two sets of ranking. When the *p* value is less than 0.05, there is significant difference between them. The results indicate that the *p* values are respectively 0.024 for NO₃-N and 0.016 for NH₄-N between Zone I^a and Zone I^b, indicating the distinct nitrogen contamination (Table 3). In order to gain the NH₄-N and NO₃-N distribution of the shallow phreatic water at a regional scale, the difference of nitrogen contamination among I^a, Zone II and Zone III are obtained. As shown in Table 3, the difference between I^a and Zone II is not distinct (*p* = 0.316 for NO₃-N and *p* = 0.12 for NH₄-N), which is consistent with the nitrogen distribution in the two zones. By

Table 2 Statistical analysis of NO₃-N and NH₄-N of samples

Index	Sample number	Min	Max	Mean	SD	Numbers of samples exceeding the limits (WHO 2011)	Numbers of samples with BDL
NO ₃ -N ^a	255	BDL	158	3.89	12.62	29	111
NH ₄ -N ^a		BDL	31.08	0.75	2.93	102	95
NO ₃ -N ^b	26	BDL	0.04	0.003	0.01	Nil	24
NH ₄ -N ^b		BDL	1.4	0.64	0.50	19	7
NO ₃ -N ^c	16	BDL	0.04	0.005	0.01	Nil	14
NH ₄ -N ^c		0.11	1.86	0.62	0.55	6	Nil

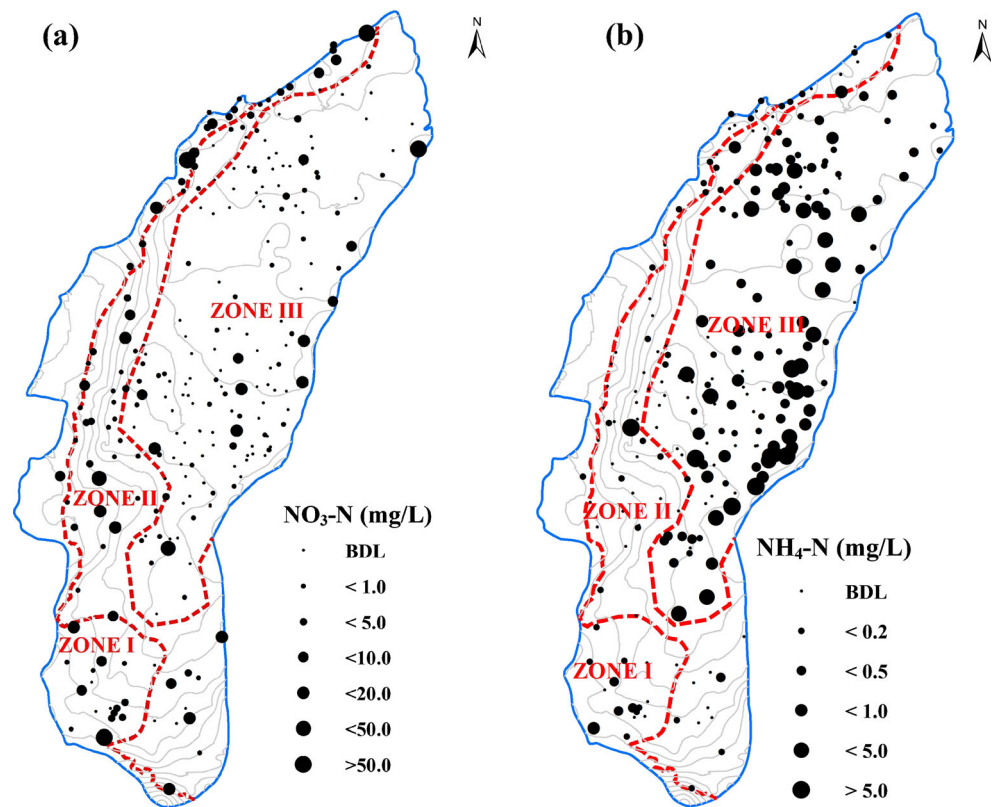
SD standard deviation, BDL below the detected limit

^a The groundwater samples from phreatic aquifer

^b The groundwater samples from the upper confined aquifer

^c The groundwater samples from the lower confined aquifer

Fig. 4 Spatial distributions of concentrations in the phreatic aquifer **a** $\text{NO}_3\text{-N}$ and **b** $\text{NH}_4\text{-N}$



contrast, the p values are all less than 0.0001 for Zone I^a–Zone II and Zone II–Zone III, confirming the distinct different nitrogen distribution among these zones.

Confined aquifers

For the water samples from the confined aquifers, Table 2 shows that $\text{NH}_4\text{-N}$ has a wider range and higher frequencies of detection than those of $\text{NO}_3\text{-N}$. Out of the 42 water samples from the confined aquifers, there are only four samples which

have $\text{NO}_3\text{-N}$ detectable concentrations. In the upper confined aquifer, the concentration of $\text{NH}_4\text{-N}$ ranges from BDL to 1.4 mg/L, with a mean of 0.64 mg/L. In the lower confined aquifer, the concentration of $\text{NH}_4\text{-N}$ ranges from 0.11 to 1.86 mg/L, with a mean of 0.62 mg/L. 59.52% of them (25 samples) with excess $\text{NH}_4\text{-N}$ (>0.2 mg/L) are not suitable for drinking. Nitrogen contamination is only observed in the regions where pumping of groundwater has been carried out. $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations are undetected in the seven monitoring wells (i.e., W2, W6, W9, S1–S3 and S9) that

Fig. 5 Variations of **a** $\text{NO}_3\text{-N}$ with well depth and **b** $\text{NH}_4\text{-N}$ and well depth. *Gray dots* denote the samples in Zone I (water sample $n = 13$), *black dots* denote the samples in Zone II (water sample $n = 28$), *blue dots* denote the samples in Zone III (water sample $n = 56$), and *red dots* denote the samples in confined aquifers (water sample $n = 35$)

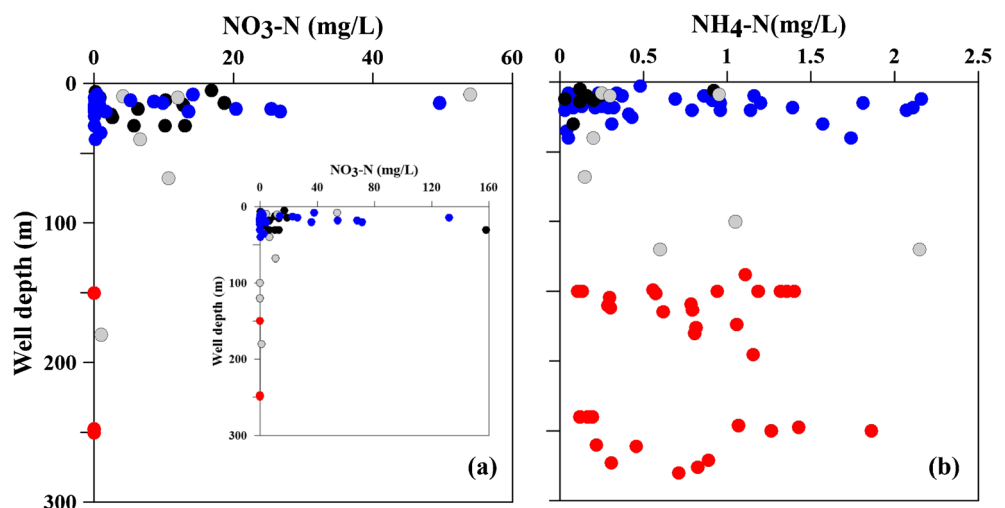


Table 3 Results of Mann–Whitney U test analysis (*p* value) (upper triangular matrix for NO₃-N, lower triangular matrix for NH₄-N)

Subpart	Zone I ^a	Zone I ^b	zone II	Zone III
Zone I ^a	–	0.024	0.316	<0.0001
Zone I ^b	0.016	–	–	–
zone II	0.12	–	–	<0.0001
Zone III	<0.0001	–	<0.0001	–

were not affected by the pumping activities. Importantly, NH₄-N predominates in the groundwater for these water supply wells.

Relations between hydrogeological properties and redox conditions

As the redox condition of water exerts a significant control on its chemistry (Ohio EPA 2014), it is necessary to understand the conditions in aquifer system. Nitrate, manganese, iron (Fe), and arsenic (As) in groundwater are often regarded as important indicators to understand redox conditions. On the basis of classification system of McMahan and Chapelle (2008), threshold values of redox indicators were 0.5 mg/L for NO₃-N and 0.1 mg/L for Fe, respectively. According to the present study and previous researches (Li et al. 2011; Han et al. 2013), low NO₃-N levels (< 0.5 mg/L) and high Fe concentrations (> 0.1 mg/L) have been observed in the phreatic water in the northern part of the study area and in the confined water, suggesting the anaerobic conditions. Meanwhile, high As concentrations (>10 µg/L) and oxidation–reduction potential (ORP) values that were also detected in the phreatic water in the northern part (Han et al. 2013) provide further demonstrations of the anaerobic environment, because the presence of dissolved As suggests that groundwater is relatively isolated from atmosphere and is not actively receiving oxygenated recharge (McMahan and Chapelle 2008; Ohio EPA 2014).

In the study area, the characteristics of hydrogeological factors are quite different along the flow path. The particle size of sediments, permeability, and groundwater flow velocity generally decrease from southwest to northeast in the phreatic aquifer (Qian et al. 2013). In such a situation, the groundwater residence time increases along the flow direction. The phreatic water at a depth of less than 60 m in the southern part of the plain has been estimated to be 6–25 years old, and for the phreatic water in the northern part of the plain has been estimated to be 45–57 years old (Wang et al. 2013). Groundwater circulates slowly and has lower renewal rates in the confined aquifers (Qian et al. 2013). In comparison to the distributions of aforementioned chemical elements, groundwater has long residence time and has a longer time to interact with electron donors in the sediments, resulting in

anaerobic conditions. Consequently, age and chemistry data are consistent with anaerobic conditions in Zone III and in the confined aquifers. The close relations between hydrogeological properties and redox conditions have been also identified in other areas (such as Landon et al. 2011; Nishikiori et al. 2012; Han et al. 2015).

Factors controlling the fate of nitrogen in groundwater

Effects of hydrogeological properties on nitrogen contamination

This investigation suggests that NH₄-N tends to occur in the groundwater in Zone I^b, Zone III and in confined aquifers. Generally, high NH₄-N concentrations beneath irrigated fields can be attributed to two mechanisms: (1) sources of NH₄-N and (2) the anaerobic and reducing conditions that activate the denitrification process and limit nitrification process in soil. In this agricultural area, urea (CO (NH₂)₂) and ammonium bicarbonate (NH₄HCO₃) are the major fertilizers applied in the fields. To maintain the yield and quality of crops, a large quantity of N fertilizer is commonly applied during cultivation. The average nitrogen fertilizer application rate per ha of cultivated land reached to 832.81 kg, which was far beyond the average rate in high fertilizer input region of China (339 kg/ha) (Chen et al. 2016). Given the high N fertilizer application and flood irrigation approach, the pollution status as reflected by NH₄-N concentrations indicates that nitrification process is limited in the groundwater that is deep and near the end of groundwater flow path under the anaerobic conditions. The two mechanisms make the N nutrients prone to leaching into the groundwater in the form of NH₄-N. Similar conclusion has been obtained in the typical agricultural catchment in central China, and NH₄-N contamination caused by N-fertilizers can also be confirmed by the chemical data (Wang et al. 2015). Unlike nitrogen fertilizer, the point-source-contamination only has a local impact on groundwater (Singh et al. 2006; Umezawa et al. 2008). Given the high variability of NH₄-N concentration in phreatic aquifer, the other potential sources such as domestic waste, sewage, and septic tanks seem to exist in the study area. Furthermore, NH₄-N were undetected in monitoring wells (W9 and S9), strengthening the rejection of contamination by organic matter in the confined aquifers.

Nitrate contamination is completely different from ammonium. NH₄-N tends to be rapidly converted to NO₃-N in aerobic environment. Consequently, NO₃-N predominates in Zone I^a and Zone II. As nitrate from different sources has characteristic δ¹⁵N and δ¹⁸O values, the isotopic compositions of NO₃⁻ are used to identify nitrate origins of groundwater and the related behavior in this paper. The isotope compositions of groundwater NO₃⁻ were detected in 36 of the 97 collected samples from phreatic aquifer. Although there is no baseline study on the estimation of natural background level of nitrate in Yinchuan

Plain, $\text{NO}_3\text{-N}$ concentration above 3 mg/L is commonly known as anthropogenic sources (Babiker et al. 2004; Kaown et al. 2009). When excluding groundwater with $\text{NO}_3\text{-N}$ levels <3 mg/L, the $\delta^{15}\text{N}\text{-NO}_3$ and $\delta^{18}\text{O}\text{-NO}_3$ values of groundwater in Zone I, Zone II, and Zone III are plotted in Fig. 6.

Measured $\delta^{15}\text{N}$ values vary from +3.94 to +19.09‰ with a mean level of +9.72‰ in Zone I and Zone II. The $\delta^{15}\text{N}$ values range from +5.70 to +28.87‰ with a mean level of 16.35‰ in Zone III. Using the $\delta^{15}\text{N}\text{-NO}_3$ values for fertilizer (-4 to +4‰) and manure or sewage (+8 to +20‰) from literature data (Kendall 1998; Böttcher et al. 1990; Fukada et al. 2003), it appears that a mixture of synthetic fertilizer and manure/sewage are responsible for the observed $\delta^{15}\text{N}$ range between +4 and 20‰. The $\delta^{18}\text{O}$ data also exhibit direct derivation from different sources (Fig. 6). Considering the typical ranges of $\delta^{18}\text{O}$ value for fertilizers (+18 to +22‰) and for manure/sewage (+0 to +8‰), the measured $\delta^{18}\text{O}\text{-NO}_3$ values (+5.93 to +21.72‰) of groundwater in the phreatic aquifer further confirm the mixing between the two different sources. Further, the isotopic compositions of nitrogen and oxygen appear to increase at a ratio of about 2:1 (Fig. 6), indicating the occurrence of denitrification. The higher mean value of $\delta^{15}\text{N}$ in the remaining nitrate in Zone III tends to indicate the more intensive denitrification occurring in the zone.

To better elucidate the effects of hydrological properties on nitrogen contamination, the changes in $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ contents along the A–A' and B–B' flow paths in the phreatic aquifer are studied (Fig. 7). Coarse sediments are highly permeable and the hydraulic gradient is steep (1–5‰) in Zone I and Zone II (Fig. 3 and Fig. 8). Under the aerobic conditions, $\text{NH}_4\text{-N}$ oxidized rapidly, and $\text{NO}_3\text{-N}$ can move easily and predominates in A1 and B1 (Zone I and Zone II). Subsequently, as the groundwater enters Zone III, the contents of fine particles (such as clayey sand and sandy clay) below

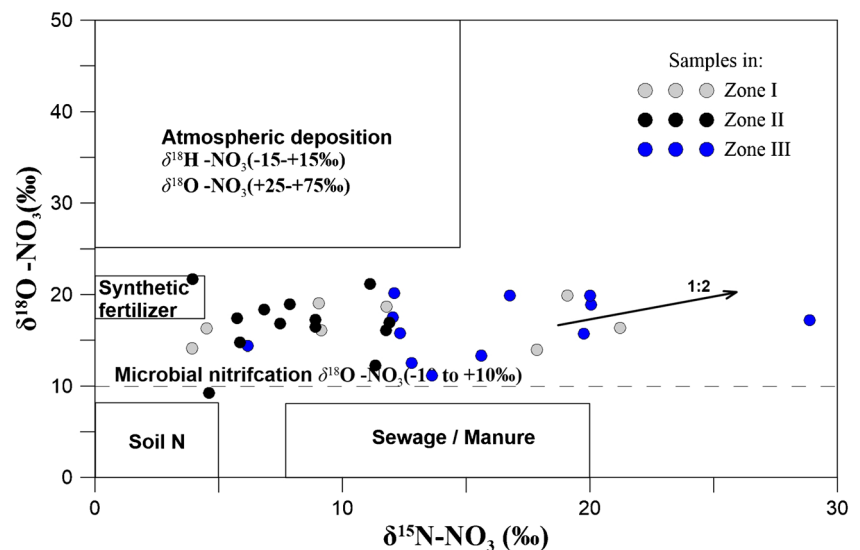
the sediments increase in the north direction and the hydraulic gradient simultaneously decreases (1–0.2‰) (Fig. 8). $\text{NH}_4\text{-N}$ that mainly derived from fertilizer is more easily to reach the water table where the depth to water is small. These conditions ensure a long resident time for the groundwater in A2 and B2–B4. Under the anaerobic conditions, $\text{NH}_4\text{-N}$ cannot to be oxidized and then become dominant in relation to the probable loss of nitrate through denitrification. Further, Fig. 8c shows that the slow water cycle in Zone III is also supported by the distribution of salinized land. All these findings indicate the major contribution of N-fertilizer on nitrogen contamination in groundwater, and the nitrogen species ($\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$) are primarily controlled by the hydrological conditions.

Influences of groundwater pumping on groundwater ammonium concentrations

The most severe consequence of intensive groundwater pumping is that the water table can be lowered. Due to the increasing vertical hydraulic gradient, pumped aquifer can be recharged by the adjacent aquifer through aquifer leakage. The situation is more likely to occur in drinking water sources and cone of depression areas (Qian et al. 2013; Wu et al. 2015a). As shown in Fig. 9, intensive extraction has caused serious decline in groundwater levels of the confined aquifers in Yinchuan plain, and a continuous decline of the water levels has been observed in recent years (Chen et al. 2015; Wu et al. 2015a). This implies that aquifer leakage from the phreatic aquifer to the upper confined aquifer or/and from the upper confined aquifer to the lower confined aquifer seems easier to occur in the pink and red areas (Fig. 9), inducing the alternation of the water chemicals.

In order to identify the effects of pumping rate on $\text{NH}_4\text{-N}$, the hypothesis is that the high $\text{NH}_4\text{-N}$ is caused by leakage

Fig. 6 Plot of $\delta^{18}\text{O}\text{-NO}_3$ values versus $\delta^{15}\text{N}\text{-NO}_3$ values for groundwater in the study area. The ranges of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ in NO_3 were from Kendall (1998) and Böttcher et al. (1990), Fukada et al. 2003 and Mayer et al. (2002). Gray, black, and blue dots denote the samples in Zone I, Zone II, and Zone II, respectively



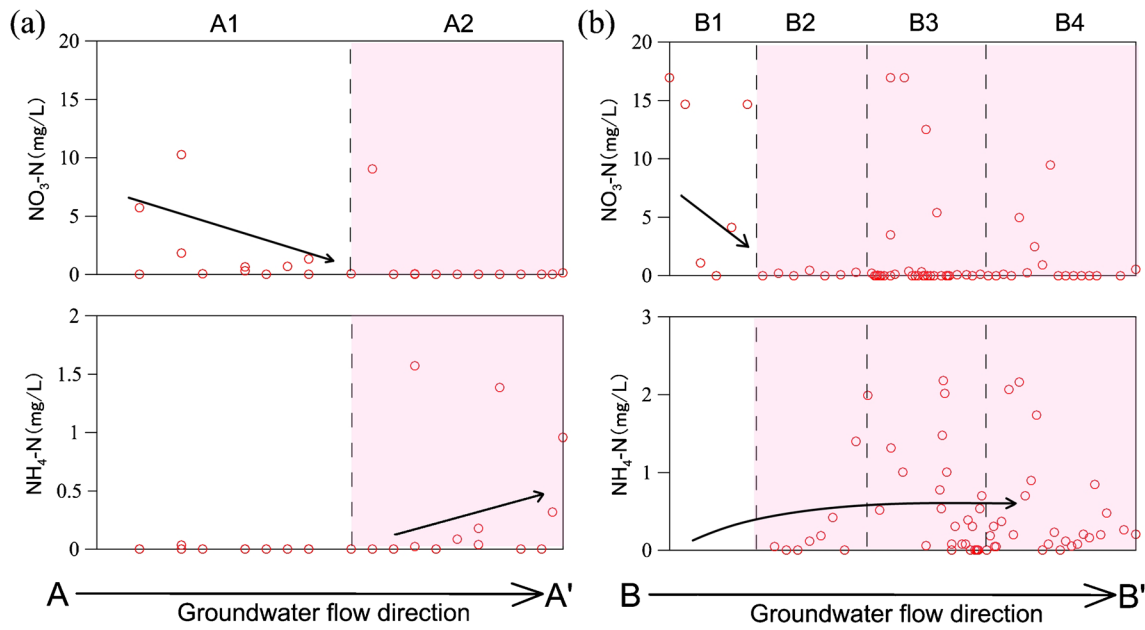


Fig. 7 Changes in $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations with groundwater flow **a** A–A' and **b** B–B'. The vertical sections of the two lines (locations of the sections are shown in Fig. 2a) are parallel to the flow directions

from the upper lying aquifer. The average concentrations of $\text{NH}_4\text{-N}$ from the water samples of the upper confined aquifer (C_{upper}) and the lower confined aquifer (C_{lower}) are shown in Fig. 10. Under the anaerobic conditions, $\text{NH}_4\text{-N}$ is the dominant form in the groundwater. Comparing $\text{NH}_4\text{-N}$ concentrations, C_{upper} and C_{lower} are close in the five water sources

(Beijiao, Nanjiao, Helan water source, and NO.1 and NO.4 water plants) within the cone of depression, where the two confined aquifers were pumped simultaneously. However, C_{lower} in Nanjiao water source is higher, which had a high pumping rates of $100,000 \text{ m}^3/\text{day}$. C_{lower} in the NO.1 and NO.4 water plants is low, which had a low pumping rate of

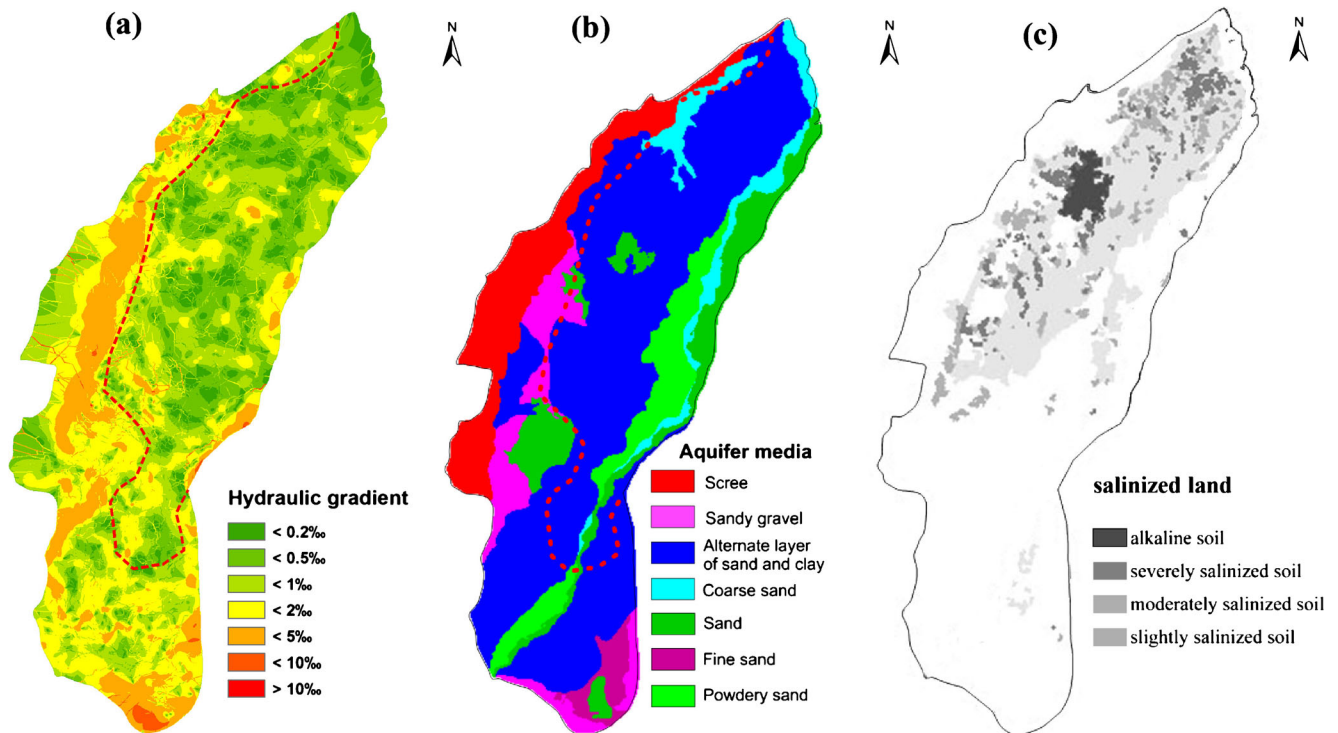
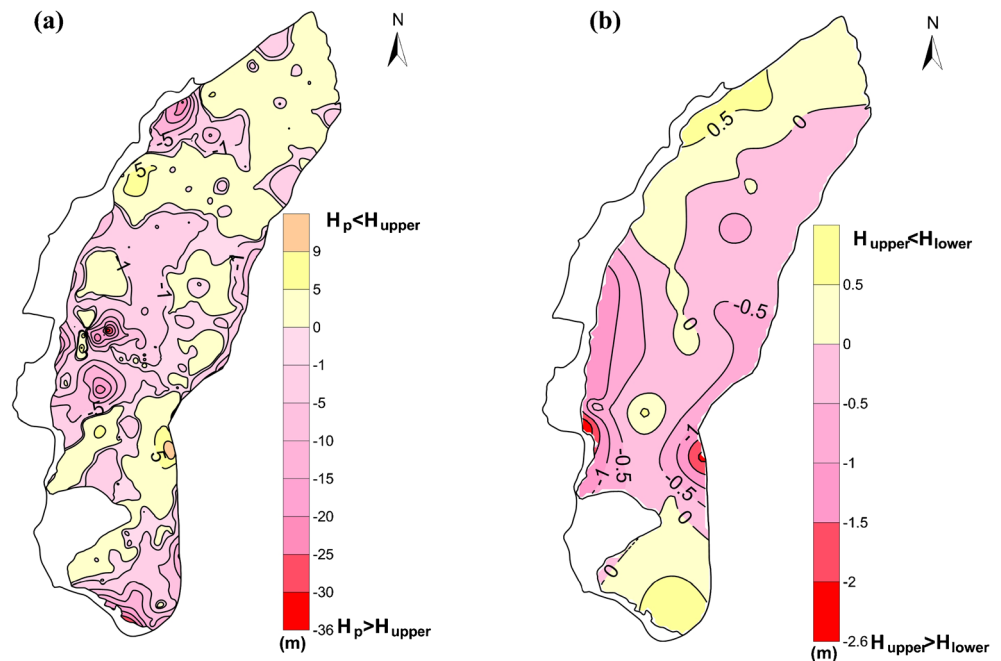


Fig. 8 Maps of **a** hydraulic gradient of water in phreatic aquifer, **b** aquifer media, and **c** salinized land (data of (b) and (c) from Qian et al. (2012))

Fig. 9 Groundwater level differences between **a** phreatic aquifer and upper confined aquifer, **b** upper confined aquifer and lower confined aquifer in 2003. H_p , H_{upper} and H_{lower} denote the groundwater levels of phreatic aquifer, upper confined aquifer, and lower confined aquifer, respectively



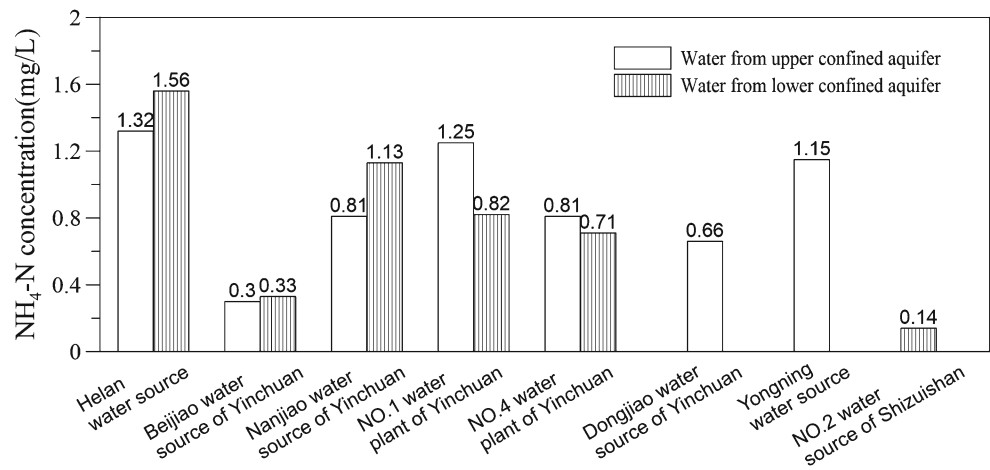
less than 30,000 m³/day. Similarly, the higher concentrations of NH₄-N in the lower confined water in the Helan and Beijiao water sources can be attributed to pumping as it had a high pumping rate of 100,000 m³/day. Therefore, even though these wells have similar depths and locate close to each other, the pumping has accelerated the downward migration of nitrogen contamination through aquitards under high pumping rate. The recent research conducted by Wu et al. (2015b) also proved the serious NH₄-N contamination in the confined water for Beijiao water source. They found that the NH₄-N concentrations varied from 0.116 to 0.362 mg/L in 14 water supply wells. The range of NH₄-N is consistent with the observation in the present study. As the groundwater is the source of drinking water for residents, the potential contamination of the water in the confined aquifers is a “time bomb”.

Even though the timing of the impending “explosion” cannot be predicted due to the insufficient evidence, it is however accelerated by the groundwater pumping.

Conclusions

The residents on Yinchuan plain depend heavily on the groundwater resource. This study has shown that there is excessive nitrogen in the groundwater, in both the phreatic aquifer and the confined aquifers. Hydrochemical, hydrogeological, and isotopic analyses have been carried out on pollution status of nitrogen in the aquifer system. The conclusions are:

Fig. 10 Comparisons of average NH₄-N concentrations for samples from the upper and lower confined aquifers



- (1) The concentrations of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in 11.37 and 40% of phreatic water samples exceed the national allowable levels of nitrogen for drinking water based on the WHO standards. In confined aquifers, 59.52% of samples are not suitable for drinking due to excessive $\text{NH}_4\text{-N}$; but $\text{NO}_3\text{-N}$ concentrations are considerably lower or undetectable.
- (2) The specific characteristics of nitrogen contamination in the aquifer system are as follows. For the single phreatic aquifer, $\text{NO}_3\text{-N}$ predominates in the shallow groundwater and $\text{NH}_4\text{-N}$ predominates in the deep groundwater. For the multilayer structure area, $\text{NO}_3\text{-N}$ predominates in the phreatic aquifer of the western and the southern parts of the plain; $\text{NH}_4\text{-N}$ predominates in the phreatic aquifer of the middle and the northern parts of the plain, and in the confined aquifers where groundwater pumping had been performed.
- (3) The distribution of nitrogen in groundwater is primarily controlled by the land use. For phreatic water, the isotopic values range from +3.94 to +28.87‰ for $\delta^{15}\text{N}$ and from +5.93 to +21.72‰ for $\delta^{18}\text{O}$, respectively. The measured isotopic values reveal that the nitrogen contamination in the phreatic aquifer is mainly contributed by the mixture of synthetic fertilizer and manure/sewage. Groundwater pumping is an important reason for the nitrogen contamination in confined aquifers due to the observed higher $\text{NH}_4\text{-N}$ concentrations in the lower confined water under higher pumping rates.
- (4) The hydrogeological properties control nitrogen fates depending on the redox conditions at a regional scale. For the phreatic aquifer at the middle and northern parts of the plain and the confined aquifers, nitrification process is limited by the longer residence time, showing anaerobic conditions in the groundwater that is deep or near the end of flow path. The occurrence of denitrification is verified by isotopic analysis in the phreatic aquifer of the middle and the northern parts of the plain.

The results of this study have advanced the understanding of the nitrogen fate in the aquifer system. They can be used as a scientific basis for developing more guidelines on groundwater monitoring and pumping programs. Given the higher $\text{NH}_4\text{-N}$ concentrations in drinking water sources, water quality deterioration may be of the greatest health concern in future. To provide more information for quantifying N cycle in the surface water–soil–groundwater system, further research in the agricultural area is sorely needed.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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