



Use of multiple isotopic and chemical tracers to identify sources of nitrate in shallow groundwaters along the northern slope of the Qinling Mountains, China

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ABSTRACT

Isotopes and major ion hydrochemistry are used to investigate potential sources of nitrate contamination in shallow aquifers along the northern slope of the Qinling Mountains, west-central China. Locally, nitrate concentrations exceed a remarkable 850 mg/L, over 40 times background levels observed in fresh mountain springs, and a knowledge and understanding of the nitrate pollution sources is essential for the development of aquifer management and protection strategies that will allow the problem to be effectively controlled. Presently, none of the suspected pollutant sources generates concentrations of nitrate that even approach levels observed in the groundwater, and this is clearly a challenge in terms of assigning responsibility for the contamination and developing appropriate management plans. However, stable isotopes of hydrogen and oxygen (δD and $\delta^{18}O$) in study area waters demonstrate that the centrally located Jijiahe Reservoir and Shidi River have been a major source of aquifer recharge in recent times and are an obvious source of the contamination. Moreover, $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ determinations suggest that, while nitrate concentrations in the river and reservoir are currently relatively low, a local, long-established fertilizer factory that has likely released high-nitrogen waste to these nearby receptors in the past, is the primary pollutant source. On a positive note, it would appear that the majority of the nitrate contamination, albeit serious in terms of drinking water quality, represents a legacy of past practice and should show gradual improvement due to modern-day environmental protection initiatives, improved equipment, better monitoring and significantly enhanced methods of wastewater treatment. However, the isotope data do indicate that the aquifer continues to be impacted by other anthropogenic activities, including agriculture and livestock raising, downstream of the industrial area and in the eastern part of the study area, meaning that monitoring and active remediation strategies need to be continued with vigilance.

1. Introduction

Nitrate contamination of groundwater associated with anthropogenic activities has been a global issue (Benkovitz et al., 1996; Keeler and Polasky, 2014; Kendall and Aravena, 2000; Stadler et al., 2008) for well over fifty years (Howard, 1985). The primary concern is that nitrate ingested through drinking water may lead to methemoglobinemia, a blood disorder that may develop following the bacterial reduction of nitrate to nitrite in the human intestinal tract (Zhang et al., 2017). Nitrite enters the blood stream and combines with the haemoglobin (Hb) to form methaemoglobin (MetHb) which diminishes the capacity of the

blood to transport oxygen (Addiscott and Benjamin, 2004; Weitzberg and Lundberg, 2013). The problem is particularly acute in very young children and babies (where the condition is often referred to as “blue baby syndrome”) as their gastric juices have a pH closer to neutrality, thus providing a better environment for nitrate-reducing bacteria to flourish. It is due to this prevailing health concern, that the World Health Organization establishes the maximum permissible limit for nitrate in drinking water at 50 mg/L (10 mg/L as NO_3^- -N). The WHO guideline for nitrite, a reduction product of nitrate, is 3 mg/L. Concern over nitrate is not limited to health. Nitrate is also widely recognized as a threat to the environment since elevated nitrate in surface water can lead to an

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excessive abundance of nutrients (known as eutrophication) which can result in the dense growth of plant life, and the death of aquatic animals due to a resulting lack of oxygen (Smolders et al., 2010).

The presence of nitrate in groundwater is normally the result of human “anthropogenic” activities. It is commonly associated with agriculture (chemical fertilizers and manure applied to cropland) (Babiker et al., 2004; Dahan et al., 2014; Liao et al., 2012; Nikolenko et al., 2018) but non-agricultural releases of nitrate (industrial effluents, atmospheric deposition of airborne industrial pollutants, and domestic sewage) are also common (Wakida and Lerner, 2005). Nitrate is highly soluble in water and migrates readily. Once it enters the aquifer system, it can remain stable for decades in oxidizing environments (positive redox potential) and can accumulate gradually where persistent sources of nitrate load the aquifer on an annual basis (Gutiérrez et al., 2018).

Managing the groundwater nitrate problem is a constant challenge. Effective management requires a knowledge of the nitrate distribution together with a full understanding of the chemical sources and the chemical transport processes (Chen et al., 2018). As a starting point, the hydrochemical characteristics of the groundwater as a function of their geological and hydrogeological setting must be established (Chen et al., 2017; Kaown et al., 2007; Schaider et al., 2016). Routinely, this can be approached using various methodologies including multivariate statistics and graphical analysis (e.g. Piper and Durov diagrams and contour maps) (Busico et al., 2018; Chen et al., 2013; Kim et al., 2009; Li et al., 2018; Matiatos, 2016; Mattern et al., 2009; Mfumu Kihumba et al., 2015). However, considerably added benefit can be derived from the stable isotopes of nitrogen, oxygen and hydrogen, which can provide more definitive indications of both water and nitrate sources (Wang et al., 2016; Stellato et al., 2016).

For example, elevated nitrate in groundwater can derive from multiple sources, each of which has experienced a unique sequence of chemical and biogeochemical processes such as fixation, ammonification, nitrification, and denitrification (Sebilo et al., 2006). The stable isotopes of nitrogen and oxygen (in nitrate) can be used to reveal those processes, thereby “fingerprinting” the source or sources (Ding et al., 2014; El Gaouzi et al., 2013; Hao et al., 2018). Xue et al. (2009) have shown the representative ranges of nitrate isotopes for different sources. The isotopic comparison between the water samples and possible sources is commonly used by many researchers to estimate the contamination sources (Li et al., 2007, 2010; Lohse et al., 2013). However, it becomes difficult to distinguish the manure and sewage which have the similar isotopic signatures (Minet et al., 2017). Good understanding of the recharge, discharge and regional groundwater flow of aquifer is also very important to reduce uncertainties (Hosono et al., 2013). In addition, boron has distinct isotopic signature in uncontaminated groundwater, seawater (De Giorgio et al., 2018) and artificial sources, such as animal manure, fertilizer and sewage (Di Fusco et al., 2017). As boron isotopes are not affected by denitrification, the combined use of $\delta^{11}\text{B}$ and $\delta^{15}\text{N}$ can provide a method to distinguish nitrate sources in groundwater and allows a semi-quantification of nitrate sources contributions (Seiler, 2005).

Stable isotopes of oxygen and hydrogen can provide a valuable insight to the origin, behavior and mixing history of the water (H_2O) in which the nitrogen compounds are dissolved and transported (Qian et al., 2007). The ^{18}O and ^2H are the intrinsic components of water molecules and retain the primary compositions of precipitation and recharge. Although groundwater retains the ^{18}O and ^2H signals of precipitation with some fidelity, it can possibly be modified by mixing of recharge of different origins. Groundwater mixing ratios based on conservative ^{18}O and ^2H are useful for understanding the major recharge of

groundwater since it commonly controls the water chemistry, allowing the nitrate sources to be further confirmed.

In the study presented here, the dual stable isotopes of nitrate ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$)¹ (Coplen, 2011) are used in combination with more conventional hydrochemical and isotope techniques to investigate sources of severe nitrate contamination of shallow groundwater in aquifers along the northern slope of the Qinling Mountains, China. This area has been subject to intense anthropogenic activity in recent decades. As environmental protection policies have been implemented, surface water quality has been remarkably improved in a short time. The subsurface environment, however, may need a longer recovery time. The knowledge and understanding of the nitrate pollution sources is essential to develop aquifer protection strategies that will allow this problem to be effectively managed. Long term monitoring is the most efficient method, but it is also challenging to use in developing areas due to the lack of monitoring system in the past. The present study focuses on providing a feasible method using integrated application of nitrate isotopes and groundwater recharge, to trace potential nitrate sources with lower uncertainties in complex groundwater nitrate issues.

2. Material and methods

2.1. Study area

This study was conducted in a 175 km² watershed located along the northern slope of the Qinling Mountains (Fig. 1). This area has a semi-humid, continental monsoon climate with a mean annual air temperature of 13.4 °C and mean annual precipitation of 580 mm. Most of the rain occurs in the wet season from June to September. Climatic data were obtained from the China Meteorological Data Service Center (China Meteorological Administration, 2018). For the hydrologic year October 1, 2012 to September 30, 2013, the year of study, precipitation at the centrally located Huaxian meteorological station was 381 mm.

The study area is bounded to the west and east, respectively by the Yuxian and Luowen Rivers. More centrally, and similarly flowing northwards from the Qinling Mountains, lies the Shidi River. This river flows for a distance 37 km before emptying into the easterly flowing Wei River which forms the boundary of the study area to the north. The Shidi River is the largest and most important of the three northerly draining rivers, and has a dominating influence on the study area groundwater flow system. Its flow rate varies seasonally, but averages 0.872 m³/s annually. Between the Qinling Mountains and the Wei River, the study area features two distinctive landforms. The first of these is a pluvial plain that borders the mountains and extends mid-way to the Wei River. Further north, an alluvial plain borders the Wei River.

2.2. Geological and hydrogeological settings

The Quaternary aquifer system contains the most important aquifers in this study area, which can be divided into alluvial aquifer and pluvial aquifer. The two aquifers are regionally interconnected and represent the primary source of groundwater for the study area's agricultural, industrial and domestic needs.

The largest reserve of freshwater in this study area occurs in the alluvial deposits. The alluvial aquifer consists of a sequence of sand and gravel with thin interbeds of silty clay. The sedimentary sequence of Quaternary alluvium forms several water-bearing units. The phreatic aquifer is composed of Middle Pleistocene to Holocene sand and gravel with the horizontal hydraulic conductivity ranging from 24 to 27 m/d. Quaternary alluvium of the shallow confined aquifer consists of Middle

¹ The measured stable isotope ratios are expressed in per mil (‰) units using delta (δ) notation relative to international standard such that $\delta_{\text{sample}}(\text{‰}) = [R_{\text{sample}}/R_{\text{standard}} - 1]$ where R_{sample} and R_{standard} are the $^{15}\text{N}/^{14}\text{N}$, $^2\text{H}/^1\text{H}$, or $^{18}\text{O}/^{16}\text{O}$ ratio of samples and standard, respectively.

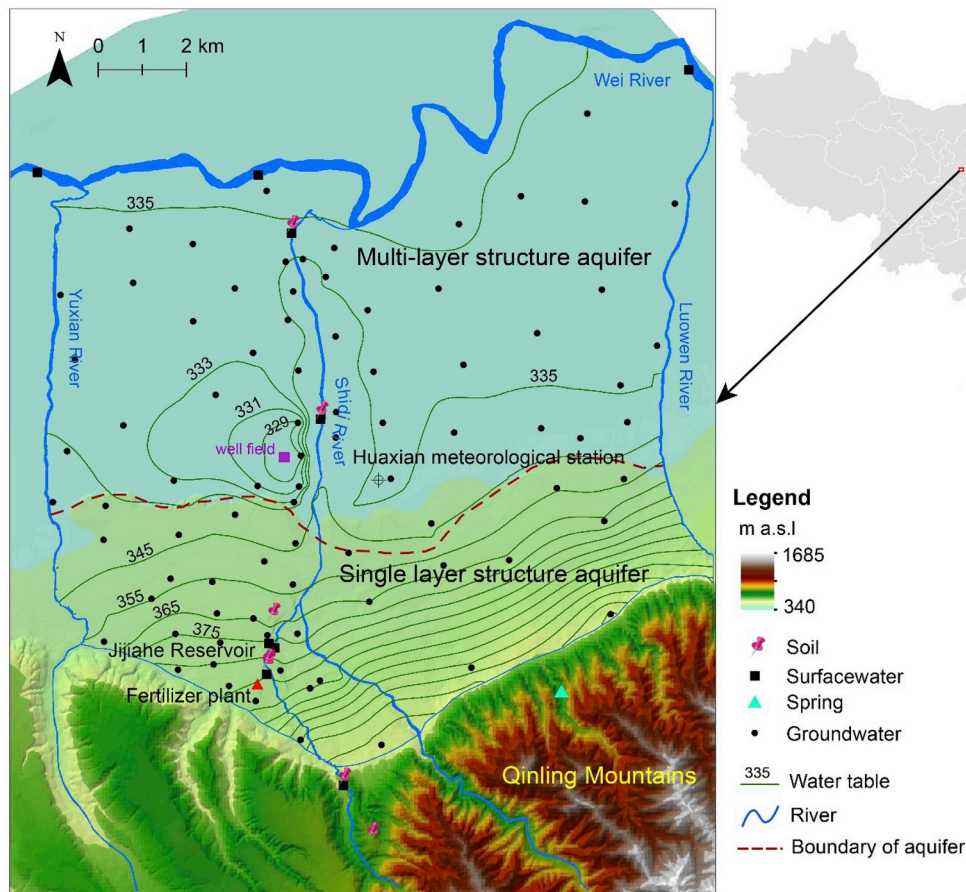


Fig. 1. Location map of the study area, showing the rivers, well field, sample sites, water table, terrain (m a. s. l. — meters above sea level).

Pleistocene alluvium and Early Pleistocene lacustrine deposit, which consists of silt, silty clay and clay with 5–10 layers interbed of fine-grained sand and medium to coarse sand. A thin layer of silty clay and silt overlies the confined aquifer and acts as its upper aquiclude. The pluvial aquifer borders the Qinling Mountains and extends mid-way to the Wei River. This Quaternary piedmont proluvium is composed of a set of about 200 m of sandy gravel and pebbles interbedded with sandy clay. The horizontal hydraulic conductivity of pluvial aquifer ranges from 2.5 to 4.7 m/d.

A water table map of the alluvial-pluvial plain aquifer was prepared by kriging interpolation of the 308 water level measurements (Fig. 1). The water table contours indicate a general movement of groundwater from the Qinling Mountains in the south, the primary source of aquifer recharge, towards the Wei River, the primary natural discharge area in the north. As shown in the water table map, it's noticeable that Shidi River tend to lose water. Furthermore, as field investigation, the embankments of Shidi River are higher than the ground surface. It can be preliminarily inferred that contaminated river water and the reservoir water would penetrate into groundwater with certain infiltration rate, though the connectivity condition of river-aquifer is not confirmed in the present study (Lamontagne et al., 2014). According to the measured data of water table depth, the thickness of vadose zone varies from 2 to 10 m in alluvial plain, with a gradual thickening from north to south. In pluvial aquifer, its thickness reaches about 20 m in the eastern piedmont area and south of the depression cone. Vadose zone is thinner in the area near the upstream of Shidi River with the thickness varying from 1 to 10 m. The vertical hydraulic conductivity of vadose zone along Shidi River varies from 3.2 m/d at the upstream, to 2.4 m/d at the midstream then continue to decrease to 0.8 m/d at the downstream (Zhang, 2014). The presence of a relatively thin vadose zone and high sediment

permeability promotes aquifer recharge, but also provides the opportunity for pollution by surface contaminant sources (Li et al., 2016a).

Locally, however, the aquifer provides water for industrial, agricultural and domestic needs, and a prominent cone of depression has developed in the center of the study area where a well field supplying industrial water to the fertilizer factory draws 1.7×10^4 m³/d. Withdrawing this water intercepts groundwater flowing towards the Wei River, causing a reversal of the natural north to south flow direction in the northern part of the study area. The well field may augment the infiltration of surface water accompanied pollutants in water.

Land use throughout much of the study area is characterized by a complex interplay of agricultural and industrial interests. As a result, non-point source pollution are possibly wide-ranging with synthetic fertilizers, wastewater and manure all capable of contributing significant amounts of nitrogen to the aquifer e.g. as nitrate. Industry is also significant locally. For example, a fertilizer factory located close to the Shidi River in its upper reaches, represents a potentially serious point source of pollution. The primary products of this fertilizer factory include synthetic ammonia, urea, ammonium phosphate and 1,4-butanediol, which has been operating over fifty years dating back to 1967.

Originally, the Shidi River was the region's primary source of water for irrigation and domestic use. In 1958, its upstream reaches were dammed close to the Qinling mountains to form the Jijiahe Reservoir with a total storage of 1.5×10^6 m³. Ever since the construction of the fertilizer factory, wastewater enriched with N compounds and coal ash was released into the Shidi River, resulting in severe pollution of the Jijiahe Reservoir.

2.3. Sample collection and laboratory analysis

In April 2013, a sampling program was conducted to investigate the hydrochemical and isotopic characteristics of the study area surface waters, spring, and groundwater and 92 samples were collected and analyzed. Additionally, groundwater levels in the phreatic aquifer were observed at 308 locations using a steel water-level gauge (SWJ-80).

Eighty-five groundwater samples were collected from pumping wells. Six samples were collected from the Shidi River, including wastewater outlets and the Jijiahe Reservoir water. A spring sample was collected in the Qinling Mountains remote from the industrial area, which can be considered to represent local groundwater in its pristine, uncontaminated state, although it may have been affected to some extent by pollutants deposited aerally.

At each sampling site, temperature, pH and total dissolved solids were measured using a portable meter (Aquaread AP-700). Samples for major ion analysis were collected using sampling protocols designed to minimize the risk of sample contamination. Precautions included multiple flushing of transfer tubes and polyethylene sampling bottles with sample water (minimum of 3 times), followed by immediate sealing and labeling of sampling containers (sample number, date, water source, water temperature, air temperature, and chemical preservatives (if added)). Samples for isotopic analysis were similarly collected but transferred to glass bottles after passage through 0.45 μm filters. All samples were stored in refrigerated coolers and transported to the laboratory within three days.

To provide additional support to the research study, soil profiles were collected to a depth of 2 m at five sites in the western part of the study area by a soil sampler (AMS). Each site was sampled at depths of 0 cm, 20 cm, 50 cm, 100 cm, 150 cm, 200 cm. In addition to, eight soil samples were collected at the surface layer along Shidi River to investigate the possible infiltration of surface water. Soil was immediately stored in sealed polyethylene bag and then kept in refrigerated coolers. Before analysis, soil was ground and filtered by 2 mm sieve. The 1 mol/L KCl was added to 5 g soil sample at a ratio of 1:10 (Li et al., 2012). The mixture was shaking for 60 min. After centrifugation the extract containing nitrate was separated and measured for NO_3^- and NO_2^- using ion chromatograph (ICS-600, Dionex).

Major ion analysis of water samples was performed at the Water and Soil Testing Center of Shaanxi Institute of Engineering Prospecting (SIEP) using approved, standard, testing methods (DZ/T0064. 1–1993; Wu and Sun, 2015). NO_3^- was measured by thymol spectrophotometry (detection limit 2.5 mg/L). NO_2^- was analyzed using diazo coupling colorimetric (detection limit 0.003 mg/L). NH_4^+ was measured by sodium reagent spectrophotometry (detection limit 0.03 mg/L). QA/QC was performed by adding duplicates during analytical procedures.

Hydrogen and oxygen stable isotopes in H_2O were determined using a Liquid-Water Isotope Analyzer (IWA-35-EP) with an analytical precision of 0.6‰ for $\delta^2\text{H}$ (VSMOW) and 0.2‰ for $\delta^{18}\text{O}$ (VSMOW). All the isotope measurements were conducted by the State Key Laboratory of Environmental Geochemistry, Chinese Academy of Sciences (CAS). In briefly, the preparation procedure for the nitrogen and oxygen isotopic analysis of nitrate was conducted using an anion exchange resin column (Fukada et al., 2004; Silva et al., 2000). At the very beginning, the dissolved NO_3^- in filtered water samples was absorbed by the anion exchange resin column. Then the NO_3^- was eluted by HCl (3 mol/L). Subsequently, the nitrate-bearing acid eluent was neutralized with Ag_2O , filtered to remove Ag_2Cl precipitate then freeze-dried to obtain solid AgNO_3 . The obtained solid AgNO_3 with the addition of Cu wire, CuO and CaO was transferred to sealed quartz tube which was heated in muffle furnace at temperature of 850 °C for 2 h according to Kendall and Grim (1990). The produced N_2 can be used for $\delta^{15}\text{N}$ analysis by mass spectrometer (MAT253). To reduce the disturbance of other non-nitrogen oxygen ions and organic matter, aliquots of the neutralized eluant for $\delta^{18}\text{O}$ analysis were processed further. Analytical procedure involves removing SO_4^{2-} and PO_4^{3-} by BaCl_2 , removing Ba^{2+} by cation

exchange resin column, removing organic matter by activated carbon column. Once these processes were completed, the obtained AgNO_3 with graphite was heated in muffle furnace at temperature of 850 °C, followed by cooling overnight. The CO_2 was extracted on a vacuum line, used for the $\delta^{18}\text{O}$ analysis by mass spectrometer (MAT253). The analytical precision was 0.2‰ for $\delta^{15}\text{N}$ (AIR) and 0.5‰ for $\delta^{18}\text{O}$ (VSMOW) (Werner and Brand, 2001).

2.4. Binary water mixing evaluations

End-member mixing analysis (EMMA) was carried out based on measured $\delta^{18}\text{O}$ values to explore the nature and degree of mixing between groundwater and the Shidi River. Application of EMMA requires that (i) the isotopic compositions of end members are both distinctive and representative, and (ii) the isotopic compositions of the mixed waters reflect only mixing and are not influenced by other processes (Li et al., 2016b).

In the present study, spring water (EM1) was selected as the groundwater end-member (value $(\delta^{18}\text{O})_G$) while surface water sample (EM2) collected at the outlet of the Jijiahe Reservoir (value $(\delta^{18}\text{O})_R$) was selected to represent the Shidi River endpoint. Where P represents the contribution of Shidi water to the groundwater system, then according to the law of mass conservation,

$$P = [(\delta^{18}\text{O})_G - (\delta^{18}\text{O})_S] / [(\delta^{18}\text{O})_R - (\delta^{18}\text{O})_S] \quad (1)$$

3. Results and discussion

3.1. Major ion hydrochemistry of water

Major ion hydrochemistry for all water samples is plotted on a Piper diagram (Fig. 2). Ca^{2+} and Mg^{2+} are the dominant cations in the groundwater, and Cl^- , SO_4^{2-} and HCO_3^- are the primary anions. For high nitrate groundwater, $\text{HCO}_3\text{-Cl-Ca-Mg}$ and Cl-Ca-Mg are the primary chemical facies. Groundwater samples with high nitrate concentrations show increased Cl^- values, suggesting strong relationship between Cl^- and NO_3^- . In the alluvial plain of the Wei River, most of the groundwater samples have NO_3^- concentration below 50 mg/L, and the $\text{HCO}_3\text{-Ca-Mg}$ is the dominant chemical facies.

Throughout the study area, the water quality is generally acceptable from a drinking water standpoint, a significant exception being nitrate (NO_3^-) which ranges up to 853.5 mg/L in the groundwater (mean value for 85 groundwater samples is 95 ± 161 mg/L). The mean value of NO_3^- in groundwater is considerably in excess of the WHO limit of 50 mg/L NO_3^- for drinking water, a value exceeded by 33 of the 85 groundwater samples. Fig. 3 shows the spatial distribution of nitrate in the shallow aquifer and demonstrates a serious cause for concern. Several “hot spots” can be observed most notably in association with the site of fertilizer plant, the Shidi River and the Jijiahe Reservoir. However, some areas, notably close to the Wei River in the north are not seriously affected.

Nitrate in Shidi River water are much lower than that in groundwater. NO_3^- concentrations vary from 15.4 mg/L at the headwater to 33.8 mg/L at Jijiahe Reservoir, increase to 35.7 mg/L at the midstream of Shidi River, then decrease slightly to 34.8 mg/L at the confluence with Wei River, resulting a mean value of 27.4 ± 8.5 mg/L ($n = 6$). The nitrate concentration in the spring sample collected in the Qinling Mountains is 20.7 mg/L and likely represents a modern-day “background concentration” for nitrate in the groundwater. This background value of groundwater nitrate may be a relatively high value, because in most cases, this value is usually less than 5 mg/L (Panno et al., 2006). In northeastern China, the concentration of NO_3^- and NH_4^+ in precipitation are higher than other sites in East Asia (Fujita et al., 2000). Chinese researchers (Tian et al., 2011) explored the chemical composition of precipitation in Xi'an that is about 70 km from the study area. The mean

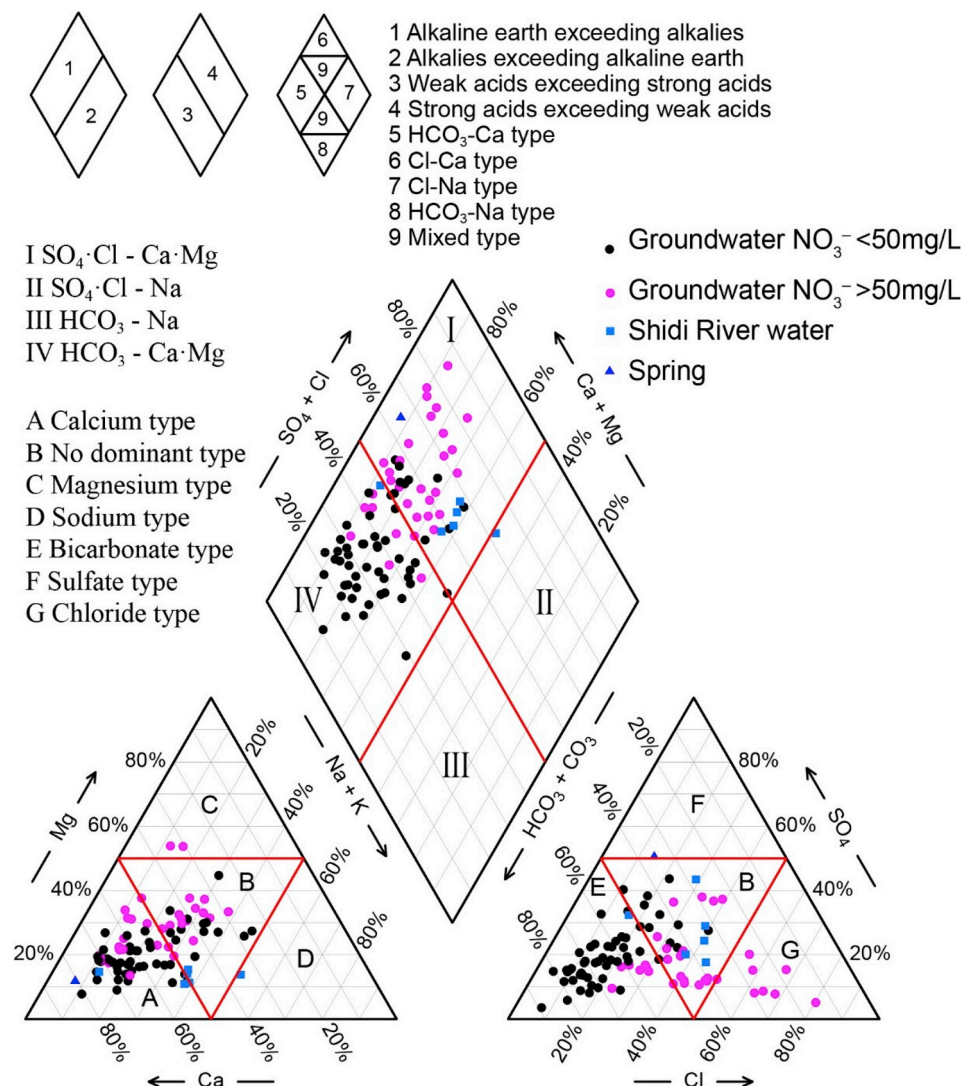


Fig. 2. Piper diagram showing the hydrochemical facies of groundwater, Shidi River water and spring samples.

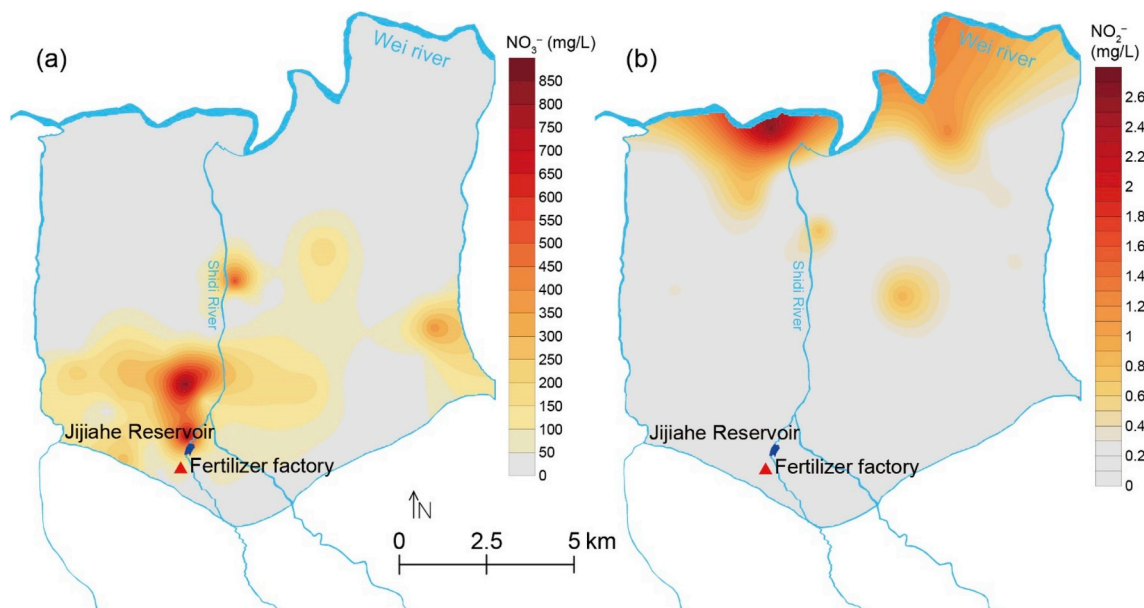


Fig. 3. Spatial distribution of (a) nitrate and (b) nitrite values of groundwater.

concentration of NO_3^- and NH_4^+ in precipitation were 5.2 mg/L and 3.2 mg/L in spring and 4.2 mg/L and 3.2 mg/L respectively in summer. The content of NO_3^- and NH_4^+ in precipitation present a high level in China. Therefore, the background value of groundwater may be affected by the atmospheric precipitation. For the purpose of this study, values in excess of 20.7 mg/L are attributed to pollution by local anthropogenic activity.

The highest groundwater NO_2^- concentration is 2.7 mg/L and is observed close to the Wei River, the natural groundwater discharge area, which is an indication of locally reducing redox conditions. It should also be noted that NO_2^- , a transitional ion in the nitrate reduction process, shows elevated concentrations (0.0–65.6 mg/L) in the Shidi River. NH_4^+ concentrations are low in the vast majority of samples from all the water groups. NH_4^+ concentrations reach 13.9 mg/L in the Shidi River water samples but for groundwater, most samples (86%) below the detection limit of NH_4^+ with a peak value of 0.5 mg/L.

In terms of nitrate pollution, the data indicate multiple potential sources. It is significant that local industry, most notably the fertilizer factory which is a major user of groundwater, returns a significant amount of the water it draws to the aquifer by discharging industrial wastewater in the groundwater recharge area. As discussed in more detail below, the nitrate distribution map (Fig. 3(a)) and Piper diagram (Fig. 2) allow broad associations to be drawn between groundwater pollution and potential sources. However, more definitive conclusions require the additional support of isotopes. The isotopes of hydrogen and oxygen in water (δD and $\delta^{18}\text{O}$) provide insight to the origins of the water, subsequent evaporative processes and mixing between the water groups, especially between groundwater and surface water in the Shidi River. Nitrogen and oxygen isotopes in the nitrate ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$) aid in the identification of the nitrate sources.

3.2. δD and $\delta^{18}\text{O}$ characteristics of study area water groups and the contribution of the Shidi River to groundwater

The stable isotopes of hydrogen and oxygen (δD and $\delta^{18}\text{O}$) are plotted for study area waters in Fig. 4. Significant features of this figure are:

- The majority of the groundwater samples plot to the right of Local Meteoric Water Line (LMWL), a displacement that indicates that most have been subjected to some degree of evaporation (Qian et al., 2014). One exception is the spring water sample that is considered to represent groundwater in a relatively pristine, “up-gradient” state which plots close to the LMWL and shows no evidence of evaporation.

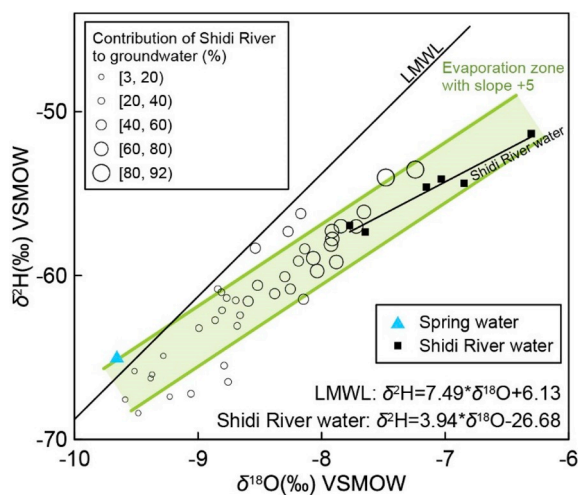


Fig. 4. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of Shidi River water samples, spring sample, groundwater samples classified by the contribution of the Shidi River.

- All Shidi River water samples lie on or close to an evaporation line (slope of +5) (Koh et al., 2010; Négrel and Petelet-Giraud, 2011; Qian et al., 2013) that emerges from a point on the LMWL close to the spring water sample.

Taking this evidence together, it must be concluded that evaporated Shidi River water represents a major source of recharge to the shallow aquifer, currently at least, if not historically.

The results of the water mixing evaluation are shown on Fig. 5. There are two members in the EMMA model, spring water (EM1 $\delta^{18}\text{O} = -9.7\text{‰}$) and the Shidi River water at upstream (EM2 $\delta^{18}\text{O} = -7.0\text{‰}$). According to the plot of $\delta^{18}\text{O}$ versus δD (Fig. 4), the $\delta^{18}\text{O}$ values of groundwater samples range from -9.6 to -7.2‰ and follow a linear relationship within the range of surface water and spring water. Therefore, a binary mixing in wells can be determined. Surface water, whether from Jijiahe Reservoir or Shidi River have enriched isotope values due to evaporation. Spring water is depleted in ^{18}O and D than groundwater since it originates further in the Qinling Mountains. The contribution of the Shidi River to the aquifer varies from just 3% (areas shown in dark green) in the area far from the river, to 92% (areas in dark red) in areas close to the Jijiahe Reservoir. Significantly, groundwater close to the industrial area receives a considerable contribution of recharge from the Shidi River and, indirectly, the Jijiahe Reservoir. The Shidi River and Jijiahe Reservoir have high oxygen isotopic values, and therefore a considerable contribution from these surface waters would elevate $\delta^{18}\text{O}$ in groundwater (Fig. 4).

Moreover, there is clearly a very strong spatial association between groundwater receiving significant amounts of Shidi River water (Fig. 5) and groundwater showing greatest enrichment in nitrate (Fig. 3(a)). If there's a dilemma to be resolved, it relates to the magnitude of the nitrate values and the fact that concentrations of nitrate in the groundwater are up to 40 times higher than concentrations observed in the Shidi River waters, i.e. the purported sources of the nitrate. In all likelihood, this can be attributed to significant improvements in the quality of the water released from these sources in recent years with values

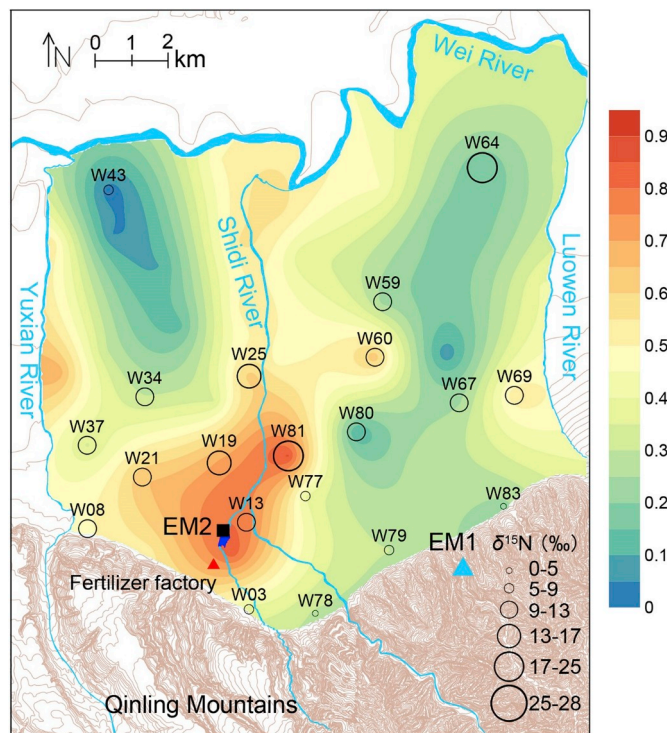


Fig. 5. Distribution map showing contribution of the Shidi River water to groundwater based on end-member mixing analysis (EMMA) and the $\delta^{15}\text{N}-\text{NO}_3^-$ values of groundwater. EM1 and EM2 are the two members in EMMA model.

currently measured very different from the past. The industrial area began operating five decades ago, long before the nitrate pollution problem became apparent.

3.3. Nitrate sources in groundwater

To provide a more definitive understanding of the nitrate source (or sources), the dual stable isotopes ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$) were investigated. Although these isotopes have been used successfully in the study of nitrate in surface water (Chang et al., 2002), their application to groundwater systems can be complicated by spatial heterogeneities in the aquifer and uncertainties with respect to groundwater pathways and rock-water physicochemical processes (Buvaneshwari et al., 2017). Factors such as land use, thickness of the vadose zone, and aquifer structure locally compound the problem, as does the characteristically slow movement of groundwater.

In the present study, the dual isotope investigation focused on NO_3^- found in four sample groups: groundwater, the Shidi River water, the soil and the mountain spring. Values of $\delta^{18}\text{O}-\text{NO}_3^-$ are plotted against $\delta^{15}\text{N}-\text{NO}_3^-$ in Fig. 6, which also displays isotope range for potential nitrate sources. The $\delta^{15}\text{N}-\text{NO}_3^-$ values in all groundwater samples vary from +2.4 to +18.9‰, and the $\delta^{18}\text{O}-\text{NO}_3^-$ values range from +11.2 to +16.8‰. Values of $\delta^{18}\text{O}-\text{NO}_3^-$ and $\delta^{15}\text{N}-\text{NO}_3^-$ of groundwater largely fit the range of Shidi River water and soil, which are the hypothesized nitrate sources. The dual isotopes of NO_3^- for groundwater are plotted linearly with the slope of 0.15 and R^2 value of 0.14 (Fig. 6), indicating the effects of denitrification in groundwater are not significant (Böttcher et al., 1990; Fukada et al., 2004). Significantly, there is a strong overlap between contaminated groundwater isotopic signature and isotopic values in nitrate from the Shidi River water, soil samples and manure. It's difficult to distinguish wastewater and manure only with comparison of $\delta^{15}\text{N}-\text{NO}_3^-$ values. However, the analysis source taking into account groundwater recharge ratio enable the source distinguishment

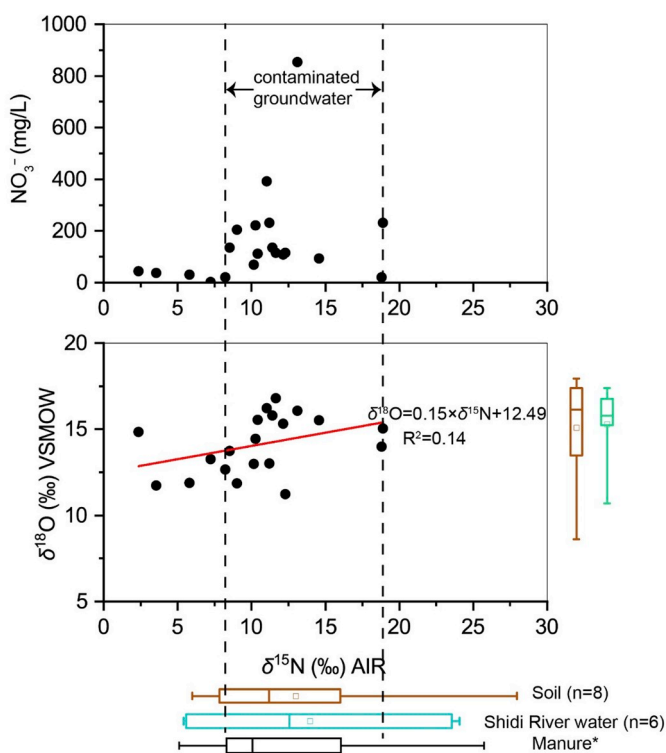


Fig. 6. Nitrate isotope comparison for groundwater samples with possible nitrate sources. Box plots showing the $\delta^{15}\text{N}-\text{NO}_3^-$ values of soil samples, Shidi River water samples and manure. The $\delta^{15}\text{N}-\text{NO}_3^-$ data of manure are cited from Xue et al. (2009).

becomes more certain. Around the industrial area and Shidi River, there is clearly a very strong spatial association between groundwater receiving significant amounts of Shidi River water and groundwater showing enrichment in $\delta^{15}\text{N}-\text{NO}_3^-$ values (Fig. 5). This suggests that wastewater release is the main nitrate source here.

To further explain the possibility of wastewater infiltration, the $\delta^{15}\text{N}-\text{NO}_3^-$ values of soil along Shidi River flow direction and surface water samples were plotted in Fig. 7. The $\delta^{15}\text{N}-\text{NO}_3^-$ values of Shidi River water show increasing trend from upstream to downstream, which are similar to the trend of soil samples, indicating the significant connection between Shidi River and soil. A sharp enrichment of $\delta^{15}\text{N}-\text{NO}_3^-$ values around the Jijiahe Reservoir can be observed in both soil and Shidi River water which may be associated with wastewater release. It's also noticeable that the $\delta^{15}\text{N}-\text{NO}_3^-$ values keep increasing and reach peak values at depression cone. Surface water sample at depression cone with higher NO_2^- concentration have higher $\delta^{15}\text{N}-\text{NO}_3^-$ composition, suggesting the occurrence of denitrification in Shidi River. The depression cone may promote the infiltration of surface water which affects the isotopic signature of both soil and groundwater. The decreasing of soil $\delta^{15}\text{N}-\text{NO}_3^-$ (+13.3‰) value at downstream may be consequence of Wei River recharge ($\delta^{15}\text{N}-\text{NO}_3^-$ value of +12.7‰).

3.4. Soil profile evidence

Strong support for the “legacy” argument is provided by the soil profile data. Fig. 8 shows soil NO_3^- profiles to a depth of 2 m for five sites in the western half of the study area. Significantly, soils close to the industrial area (TK2 and TK4) reveal very high NO_3^- concentrations (225 mg/kg at the surface of TK4 and averaging ~ 100 mg/kg throughout TK2). Moreover, while most of the profiles show a decline in NO_3^- with depth, probably reflecting the role of denitrification, TK2, the site closest to the SHG industrial plant, shows a distinctive spike at a depth of 50 cm. This is likely a remnant of past activities when releases of NO_3^- to the subsurface were considerably higher than present. It should also be noted that relatively high NO_3^- values (50–150 mg/kg) present in some of the shallow samples remote from the industrial area, indicating that industry is not the sole source of nitrate in the region and that sources such as recharge from the Wei River, agriculture and livestock raising may also be significant locally.

All soil profile samples show low nitrite concentrations, and the NO_2^- concentrations in top-layer soil are 0.10 mg/kg and 0.19 mg/kg at TK2 and TK4, respectively, increasing to 0.47 mg/kg at TK6 and 0.53 mg/kg at TK7. The maximum NO_2^- concentration in the top-layer soil is observed at TK8 (0.58 mg/kg), suggesting that denitrification is

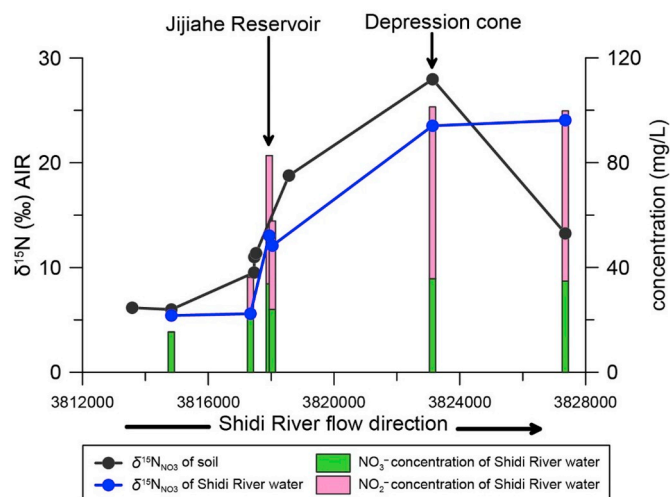


Fig. 7. Variation of $\delta^{15}\text{N}-\text{NO}_3^-$, NO_3^- and NO_2^- values in soil and surface water along Shidi River flow direction.

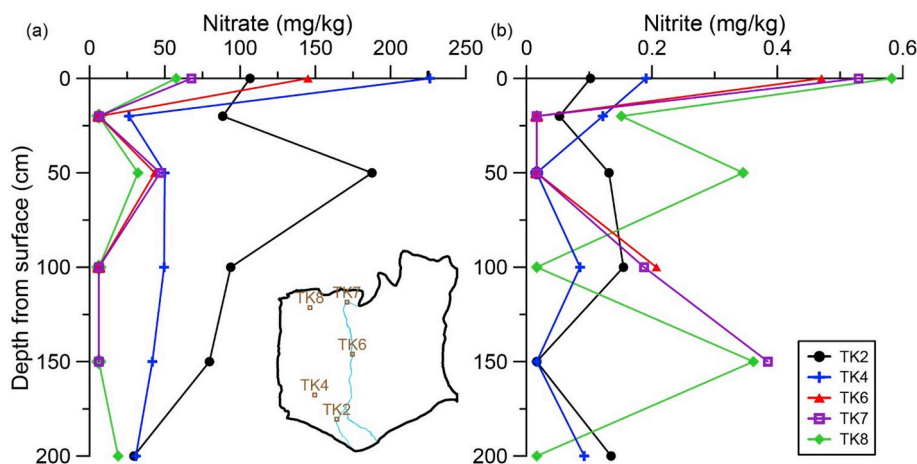


Fig. 8. Soil nitrate and nitrite profiles with sampling depths of 0.2 m, 0.5 m, 1 m, 1.5 m, and 2 m.

significant in the discharge area. Vertically, the NO_3^- values fluctuate strongly with depth. In TK2, the NO_3^- value decreases to a depth of 0.2 m, and then increases to a depth of 2 m, indicating no remarkable recent nitrate inputs and higher nitrate inputs from the past. In other sites, the nitrite values show decreasing overall trends with depth, which could be associated with recent inputs from other nitrate sources (surface water recharge and agriculture).

3.5. Potential for the future

The results indicate that unusually high NO_3^- levels observed in study area groundwaters are a legacy, largely associated with the historical release of untreated industrial wastewater. However, the regional distribution of nitrate (Fig. 3(a)) clearly shows that other sources of nitrate play a role locally. It is significant for example, that while the Shidi River and Jijiahe Reservoir represent major sources of infiltration to the aquifer (Fig. 5) and need to be monitored very closely, many wells receiving a large component of their recharge from these surface sources, are surrounded by a wide range of pollutant sources, each capable of loading the aquifer with additional point and non-point sources contaminants (Lockhart et al., 2013). This is illustrated by Fig. 5, which shows several samples (W64, W59, W80, W67) receiving small amounts of Shidi River water present high $\delta^{15}\text{N}-\text{NO}_3^-$ values. Sources include chemical fertilizers used in agriculture and fruit production, livestock raising, and various industrial wastes. Although the isotope data suggest that fertilizer sources together with nitrate in manure has not played a significant role in wide range, continued degradation due to these sources could seriously delay the rate at which groundwater quality recovers in the future. Therefore, it is highly recommended that N-fertilizer application should be controlled to reduce nitrogen leaching rates. Manure should be regulated and stored in specified places.

In the long-term, the control of N inputs and implementation of remediation strategies will lead to improvement of this environment issue. However, due to lack of historical data, although improvements in the regulation of wastewater discharge, there is a degree of speculation on the future groundwater quality. The obtained results indicate that natural attenuation through denitrification in groundwater is insignificant. The high-level nitrate contaminants resulted by historical wastewater discharges can produce long-term effects on groundwater quality, and the timescale and degree of future attenuation can be significant (Wang et al., 2019). Hence, more quantitative researches are needed to improve understanding of the mechanisms of nitrogen leaching and nitrogen accumulation characteristic in soil and therefore support effective groundwater management. Recognizing this, continued vigilance and more active strategies are essential. More efficient and water-saving irrigation scheme should be implemented to weaken the

leaching of irrigation return flow. Groundwater exploitation should be managed strictly with the consideration of water balance to control the groundwater recharge areas and water pathways. These strategies will allow for better control on contamination inputs and monitoring on the groundwater quality trajectory.

4. Conclusions

Serious nitrate contamination of shallow aquifers along the northern slope of the Qinling Mountains, west-central China was investigated using a combination of major ion hydrochemistry and stable environmental isotopes. The isotopes of hydrogen and oxygen in water (δD and $\delta^{18}\text{O}$) were used to help establish the origins of the water, the role of evaporation and ground-surface water mixing, while nitrogen and oxygen isotopes in the nitrate ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$) were used to help identify the nitrate sources. The purpose of the study was to develop an understanding of the nitrate pollution issue as an essential pre-requisite for the development of aquifer management and protection strategies that will allow the problem to be resolved.

The study found that none of the suspected pollutant sources could account for the unusually high levels of nitrate observed in the groundwater (locally in excess of 850 mg/L), and this represented a difficult challenge in terms of assigning responsibility for the contamination. However, isotopic evidence demonstrated that the centrally located Jijiahe Reservoir and Shidi River to be a major source of aquifer recharge in the area most seriously affected by nitrate, and was therefore an obvious conveyance of the contamination. Furthermore, $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ data confirmed that wastewater discharge from a nearby, long-established fertilizer factory to be the primary source of the nitrate contamination, the vast majority of the release occurring in the past when environmental regulations were considerably more lax than they are today. However, available do indicate numerous other potential sources of nitrate pollution exist in the area, and these represent an emerging, if not ongoing, threat to groundwater quality. It is essential, therefore, that environmental monitoring and more active remediation strategies be continued with vigilance.

Declaration of competing interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2019.104512>.

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