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Relationship between land-use and sources and fate of nitrate in groundwater in a typical recharge area of the North China Plain

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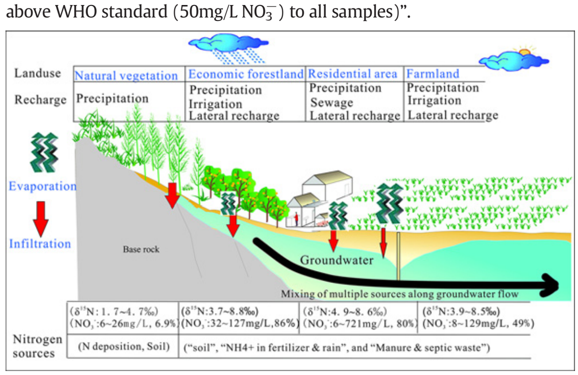
HIGHLIGHTS

- We investigated the impacts of diverse land use on nitrate in groundwater.
- Multivariate statistics methods were combined to identify source of nitrate.
- Manure and septic waste were dominant sources for groundwater with high nitrate.
- Lack of de-nitrification highlights the importance of controlling nitrate sources.

GRAPHICAL ABSTRACT

"(δ^{15}N:1.7 ~ 4.7‰)" means range of nitrate isotopes;
"(NO_3^-:6~26mg/L, 6.9%)" means "(Range of NO_3^- Concentration: 6~26mg/L, Percent of samples with nitrate concentration above WHO standard (50mg/L NO_3^-) to all samples)".



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ABSTRACT

Identification of different nitrate sources in groundwater is challenging in areas with diverse land use and multiple potential inputs. An area with mixed land-uses, typical of the piedmont-plain recharge area of the North China Plain, was selected to investigate different nitrate sources and the impact of land use on nitrate distribution in groundwater. Multiple environmental tracers were examined, including major ions, stable isotopes of water (δ^2H-H_2O, δ^{18}O-H_2O) and nitrate (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-). Groundwater was sampled from four land-use types; natural vegetation (NV), farmland (FL), economic forestland (EF) and residential areas (RA). A mixing model using δ^{18}O and Cl^- concentrations showed that groundwater recharge predominantly comprises precipitation and lateral groundwater flow from areas of natural vegetation in the upper catchment, while irrigation return water and wastewater from septic tanks were major inputs in farmland and residential areas, respectively. Land use variation is the major contributing factor to different nitrate concentrations. In total, 80%, 49% and 86% of samples from RA, FL and EF, respectively exceeded the WHO standard (50 mg/L NO_3^-), compared to 6.9% of samples from NV. Isotopes of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- verified that nitrate in groundwater of the NV (with δ^{15}N ranging from 1.7‰ to 4.7‰) was sourced from soil and precipitation. Examination of δ^{15}N-NO_3^- vs δ^{18}O-NO_3^- values along with multivariate statistical analysis (principle component and cluster analysis) helped identify sources with overlapping isotopic values in other land-use areas (where δ^{15}N values range from 2.5‰ to

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10.2‰). Manure and septic waste were dominant sources for most groundwater with high NO_3^- and Cl^- concentrations in both farmland and residential areas. The lack of de-nitrification and fact that the area is a recharge zone for the North China Plain highlight the importance of controlling nitrate sources through careful application of manure and fertilizers, and control of septic leakage.

1. Introduction

Changes in land-use patterns have dramatically affected groundwater quality in many parts of the world, altering inputs of water and contaminants from the surface, changing recharge sources and mechanisms, and affecting biogeochemical processes in the unsaturated zone (Tran et al., 2010;Wilson, 2015). Nitrate in groundwater can be of natural or anthropogenic origin; although background levels in areas that are relatively un-modified by human activity typically don't exceed 5–10 mg/L (or 1–2 mg/L as NO_3-N; Panno et al., 2006). Several studies have shown that nitrate contamination in groundwater is strongly correlated to land use and anthropogenic activities (e.g., Xue et al., 2009; Dubrovsky et al., 2010). McLay et al. (2001) found that while non-point source groundwater nitrate contamination may reflect widespread intensive agricultural practices, localized site-specific factors typically affect nitrate in shallow groundwater to an equal or greater degree. Common sources of groundwater include soil-N, manure, synthetic fertilizers, waste water from leaking sewerage networks or septic systems (e.g. Heaton, 1986; Kendall, 1998), as well as specialized sources such as residues from weapons testing (Bordeleau et al., 2008). Processes at the surface or soil zone may also be important – e.g. Lockhart et al. (2013) found that elevated nitrate levels strongly correlated with a combination of shallow water tables and the presence of surface sources (animal feeding operations or horticulture). Different cultivating practices (Rankinen et al., 2008) and manure management practices (Lord et al., 2002), precipitation surpluses (Salo and Turtola, 2006), water quality of wastewater irrigation (Tang et al., 2006) and rates of denitrification (linked to soil organic matter, redox conditions and microbial activity) also heavily influence the concentrations of nitrate leached into aquifers (Wankel et al., 2009). Consequently, land-use patterns to a strong degree determine groundwater nitrate concentrations, in combination with hydrogeological and biogeochemical controls.

Identifying nitrate sources is the key step to reducing groundwater pollution with nitrate. Nitrate sources are known to exhibit characteristically different isotopic $\delta^{15}N$ and $\delta^{18}O$ values (Chang et al., 2002; Xue et al., 2009; Kaown et al., 2009; Widory et al., 2013; Gooddy et al., 2014; Popescu et al., 2015). Hence, the determination of $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- in water samples can provide meaningful insight into nitrate origins in water. However, dual isotope analyses alone do not always provide conclusive information about sources and the processes that nitrate has undergone in aquifer systems. Uncertain and variable isotopic signatures of localized sources, overlap between isotopic values of different sources, mixing between nitrate of different origins, and changes in isotopic signatures due to biogeochemical processes may all complicate source identification based on isotopic signatures alone. Hence, other chemical and hydrogeological information should be simultaneously used to interpret the sources and biogeochemical history of NO_3^- in aquatic systems (Mayer, 2005). In recent years, researchers have combined multivariate statistical analysis methods with isotopes of nitrate and isotope mixing models to deal with these uncertainties and better delineate possible sources (Xue et al., 2012; Xue et al., 2013; Kim et al., 2015; Matiatos, 2016).

It is widely recognized that the North China Plain (NCP), a focal point for both intensive agriculture and intensive heavy industry, with a population of hundreds of millions of people, is the location of some of China's biggest water and other environmental challenges. In recent years, nitrate (NO_3^-) contamination of groundwater has become a growing concern for people in rural areas in the NCP, where it is used as drinking water (Zhu and Chen, 2002). Nitrate has not only been found in the shallow groundwater system of the NCP but also in the deep aquifers, due to rapid bypass flow along wells or other conduits (Currell et al., 2012;Han et al., 2016). It has been reported that the average NO_3^--N concentrations are in general significantly higher in agro-ecosystems (4.1 ± 0.33 mg/L) than forest ecosystems (0.5 ± 0.04 mg/L) (Zhang et al., 2013). In recent years, most research on nitrate in the NCP has focused on groundwater in the plains areas, including the alluvial fans, major cities and coastal areas. In these areas land use is generally homogeneous over wide areas, and is either urban (e.g. large cities and towns), or extensive large-scale farmland (encompassing small rural residential areas). Nitrate from diffuse agricultural sources, such as fertilizer over-application and wastewater irrigation is thought to be the major cause of widespread nitrate pollution in the shallow groundwater in these areas (Chen et al., 2006; Tang et al., 2006; Wang et al., 2013;Zhang et al., 2016). Leakage from septic tanks and polluted rivers also locally results in high nitrate concentrations in the urban areas (Wang et al., 2014; Yin et al., 2016).

However, there are few studies reporting nitrate contamination in the hilly areas of the North China Plain, which are particularly important as they represent the major sources of recharge to the wider aquifer system (Cao et al., 2016). These hilly areas, in the transition from the Taihang Mountains to the plains of the NCP, are typically characterized by more diverse mixed land-use, including natural vegetation, forest, farmland and residential areas. Given the importance of these areas as major recharge sources for the plains, identifying the impact of different land-use activities and determining sources of nitrate is of particular importance. Anthropogenic activities such as farming, irrigation and urban development have recently intensified in these areas, which may have wider implications for water quality in the broader NCP. Wang et al. (2016) reported that land use variation during groundwater recharge is the major factor affecting nitrate concentrations in groundwater of such hilly areas, considering the (relatively young) age of the groundwater recharge. However, the contribution of each land use to nitrate load in groundwater has not been clearly understood or documented in these areas. Investigating the sources and fate of nitrate in groundwater and their relationship to land-use are therefore critical for groundwater resource safety both locally and regionally.

The objective of this study was to determine the impact of land use on nitrate sources, fate and distribution in a typical catchment located in the recharge area (transition zone between hill and plains area) of the NCP, China. We used dual-stable isotopes of nitrate and water, along with multivariate statistical analysis and other hydrochemical and hydrogeological data, to identify and trace sources of nitrate related to different land use patterns. The study provides valuable information for land and water management that can be used to help minimize nitrate contamination in this important region of groundwater recharge.

2. Materials and methods

2.1. Description of the study area

The study area is located in Yuanshi County (37°45′ ~ 37°54′ N,114°14′ ~ 114°34′E), which is typical of the transition zone from hilly areas of the Taihang Mountains to the plain areas of the NCP