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Determination of nitrate contamination sources using isotopic and chemical indicators in an agricultural region in China

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ABSTRACT

Stable isotopic measurements ($\delta^{15}N$ and $\delta^{18}O$), combined with hydrochemical assessment, were used to elucidate the chemical quality of groundwater and the sources of nitrate (NO_3^-) in the groundwater in an agricultural region at Huzhou City, China. Paddy rice (Zhejing 41) and vegetables (Chinese cabbage) are the typical crops grown in the study area. The chemical properties of groundwater in the study area were controlled using natural geochemical processes and anthropogenic activities. The results show that SO_4^{2-} and NH_4^+ were the major contaminants. Surficial conditions influenced the shallow groundwater. However, no relationship between the ion concentration in groundwater and well depth was found. The combined use of isotopes was useful for identifying NO_3^- sources. The isotopic values for $\delta^{15}N$ and $\delta^{18}O$ ranged from −0.8‰ to 20.8‰ and from −2.0‰ to 18.8‰, respectively. The isotopic data were definitive and revealed that N-fertilizer, soil organic matter, and manure dominated the sources of NO_3^- in the study area. The $\delta^{15}N$ and $\delta^{18}O$ data for NO_3^- indicated a significant degree of nitrification and a lesser extent of denitrification in the agricultural area. Spatial variations in $\delta^{15}N$ for NO_3^- showed that NO_3^- concentration and $\delta^{15}N$ values in the upper groundwater (<200 cm) were higher than the values in the lower groundwater (>200 cm).

1. Introduction

Nitrate (NO_3^-) contamination of groundwater is a pervasive problem in many parts of the world. If groundwater is used for drinking, high NO_3^- concentration could cause various diseases, including methemoglobinemia (O'Riordan and Bentham, 1993; Panno et al., 2001). Possible sources of NO_3^- contamination include manure applied to land, chemical fertilizers, industrial effluent, domestic wastewater, septic systems, human waste lagoons, animal feedlots, native soil organic matter, and geological sources (Helmut, 2000; Xue et al., 1996). NO_3^- can leach from all the sources mentioned above into the groundwater because NO_3^- is very mobile in most soils (Nolan, 1999; Sun et al., 2005; Choi et al., 2007). The high applications of N-fertilizers and various animal waste fertilizers in agricultural areas are the most common anthropogenic sources of NO_3^- contamination of groundwater (Liu et al., 2005). However, ascertaining which of these sources contribute to NO_3^- in groundwater is generally difficult. Therefore, the determination of the sources of NO_3^- in groundwater is the primary and is an important step in the process for improving groundwater quality. This process can possibly facilitate the reduction of the amount of NO_3^- discharged into water bodies.

The N and O isotopic ratios of NO_3^- have been widely used for providing more conclusive information in evaluating the sources of NO_3^- in water (Komor and Anderson, 1993; Deutsch et al., 2005; Seiler, 2005; Xue et al., 1996; Hosono et al., 2011). Numerous NO_3^- sources have distinct isotope signatures, and the processes that control isotopic composition are widely known (Kendall, 1998; Mayer et al., 2002; Seiler, 2005). Nitrogen is composed of two stable isotopes with atomic masses of 14 and 15, respectively. For example, the majority of N in the atmosphere are composed of ^{14}N (99.634%) and the remainder are composed of ^{15}N (0.366%) (Junk and Svec, 1958). Oxygen is composed of three stable isotopes with atomic masses of 16, 17, and 18, respectively. The majority of O in the atmosphere are composed of ^{16}O (99.759%), ^{17}O (0.037%), and ^{18}O (0.204%) (Cook and Lauer, 1968).

Researchers use isotopic ratios expressed in delta (δ) units and per mil (‰) notations relative to the respective international standards. Isotropic ratios are defined as follows: $\delta_{sample} = [(R_{sample} - R_{standard})/R_{standard}] \times 1000$, where R is the $^{15}N/^{14}N$ or $^{18}O/^{16}O$ ratio of the sample and standard for $\delta^{15}N$ and $\delta^{18}O$, respectively. $\delta^{15}N$ values were reported to be relative to atmospheric air (AIR), and $\delta^{18}O$ values were reported to be relative to the Vienna Standard Mean Ocean Water (VSMOW).

Different NO_3^- sources can be discriminated from different $\delta^{15}N$ values. In general, NO_3^- derived from precipitation has $\delta^{15}N$ values in the range of −13.0‰ to 13.0‰. $\delta^{15}N$ values of chemical fertilizers range from −7.4‰ to 6.8‰; the typical $\delta^{15}N$ values of soil N

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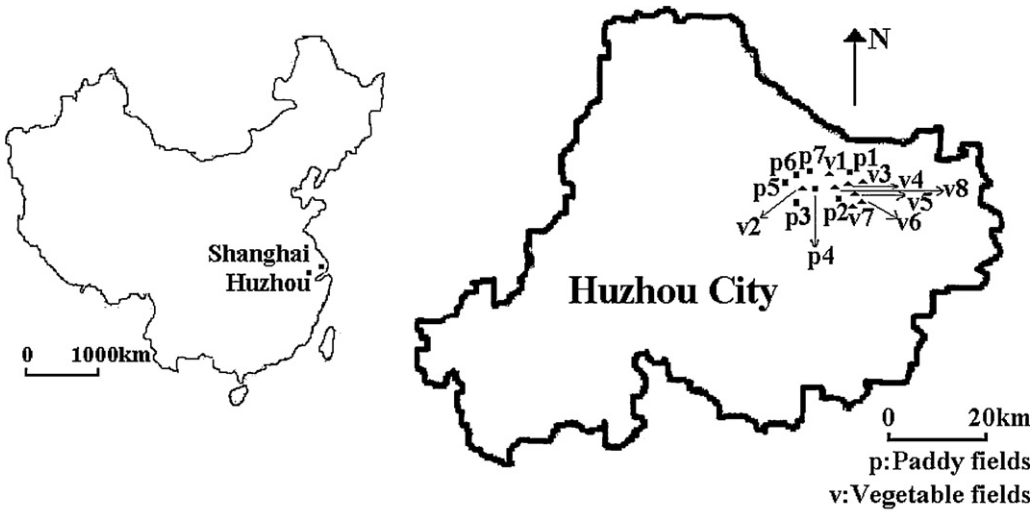

Fig. 1. Geographic location of the study area, Huzhou City.

range from −3.0‰ to 8.0‰; NO_3^- derived from manure has $\delta^{15}N$ values in the range of 5.0–25.0‰; and the $\delta^{15}N$ values of NO_3^- originating from sewage range from 4.0‰ to 19.0‰ (Hübner, 1986; Kellman, 2005; Piatek et al., 2005; Bateman and Kelly, 2007; Choi et al., 2007; Li et al., 2007; Singleton et al., 2007; Lee et al., 2008; Zhang et al., 2008; Chae et al., 2009; Xue et al., 1996; Koh et al., 2010; Hosono et al., 2011). The variability of $\delta^{15}N$ values within a single source type may affect its ability to distinguish one source from another, thus the mixing and exchange of nitrogen among different nitrate sources can occur. Significant overlap in the nitrogen isotopic compositions of chemical fertilizers, soil organic matter, or atmospheric deposition and sewage/manure makes the differentiation among these nitrate-nitrogen (NO_3^--N) sources difficult, particularly when only the nitrogen isotope values are used. Studies also found that $\delta^{15}N$ values were not rigidly effective because nitrogen isotopes can be fractionated during transport through the unsaturated zone or aquifer. For example, denitrification and dissimilatory nitrate reduction are microbially mediated and should result in ^{15}N-depletion in products and ^{15}N-enrichment in reactants. Progressive denitrification or dissimilatory nitrate reduction should decrease nitrate concentrations and increase $\delta^{15}N_{NO_3}$ values (Heaton, 1986; Smith et al., 1991; Panno et al., 2001). Therefore, $\delta^{18}O$ values of NO_3^- were analyzed in the current study to determine the sources of NO_3^- in the study area. As a result, $\delta^{18}O$ values were found to be more useful than the $\delta^{15}N$ values in separating atmospheric NO_3^- deposition from microbially produced soil NO_3^- and synthetic NO_3^- fertilizers from other NO_3^- sources (Mayer et al., 2002; Deutsch et al., 2005). NO_3^- derived from nitrification has $\delta^{18}O$ values in the range of −10.0‰ to 10.0‰ (Kendall, 1998; Fukada et al., 2004). The $\delta^{18}O$ values of atmospheric NO_3^- show a range of 25.0–75.0‰ (Kendall, 1998; Lee et al., 2008). NO_3^- from fertilizers has distinctive $\delta^{18}O$ values in the range of 17.0–25.0‰ (Kendall, 1998; Singleton et al., 2007).

A number of studies have shown that $\delta^{15}N$ and $\delta^{18}O$ values are useful for discriminating NO_3^- sources in groundwater (Heaton, 1986; Aravena and Robertson, 1998; Panno et al., 2001; Kellman and Hillaire-Marcel, 2003; Jin et al., 2004; Seiler, 2005; Liu et al., 2006; Xue et al., 1996; Koh et al., 2010; Hosono et al., 2011). The summary of the literature showed that $\delta^{15}N$ and $\delta^{18}O$ values in groundwater had big ranges because of the different NO_3^- sources. For example, investigations in South Korea showed that groundwater from paddy-cultivated areas had $\delta^{15}N$ values in the range of −0.4‰ to 21.0‰ and $\delta^{18}O$ values in the range of 0.0–29.0‰; groundwater from residential areas had $\delta^{15}N$ values in the range of 2.9–11.8‰ and $\delta^{18}O$ values in the range of 1.1–5.0‰ (Koh et al., 2010). Another study in southern Ontario, Canada found that the groundwater from residential areas (septic system) had $\delta^{15}N$ values in the range of 6.0–58.3‰ and $\delta^{18}O$ values in the range of 1.6–12.8‰ (Aravena and Robertson, 1998). It was not surprising that land use was the dominant factor that controlled nitrate pollution because most groundwater nitrate contaminations originate from the vertical transport of a source from the soil profile.

Over 35% of the sampled wells at some agricultural areas in Zhejiang Province, China exceed the recommended limit of 10 mg NO_3^--N L^{-1} (Dong, 2001; Jin et al., 2004; Zhang et al., 2008). Manure and fertilizer were found to be the major NO_3^- sources in the groundwater of agricultural areas. Therefore, identifying the major sources of NO_3^- in groundwater would help water managers and planners in developing measures to reduce groundwater contamination from NO_3^-. Moreover, careful management of fertilizer and manure uses is necessary to minimize NO_3^- concentration in groundwater. From 2003, the uses of manure and fertilizers in the agricultural areas of China were controlled. Some projects, such as measuring the soil nutrient and using fertilizers according to soil nutrients programs, were implemented to effectively control the use of fertilizers. Another effective project was controlling the biggest fertilizer in different crop systems plan. Fertilizer control projects have implemented a few years. A question whether NO_3^- in the groundwater of agricultural areas in Zhejiang Province, China has decreased has been raised. Based on these, the current study aims to analyze hydrochemical data and their vertical spatial variations collected in two different cropping systems (single paddy cropping system and vegetables cropping system), and consequently clarify the origin of NO_3^- and biogeochemical processes in an agricultural region of east China.

2. Materials and methods

2.1. Description of the study area

The current study investigated an agricultural area in Huzhou City in east China. The study area, which lies few meters above sea level, was built on the marine, estuarine, and fluvial alluvium of the Yangzi River (Fig. 1), and has limestone as the dominant rock type. Vertical percolation of rain and floodwater are the sources of ground water recharging in Huzhou. Shallow groundwater is contained in the alluvium deposits and has a free water table 1–6 m below the surface, in which groundwater flow is relatively static.