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Tracing nitrate pollution sources and transformation in surface- and ground-waters using environmental isotopes

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HIGHLIGHTS

- Nitrate sources in surface and groundwater were identified by multiple isotopes.
- Nitrate pollution displayed obvious seasonal variations.
- Nitrate of surface water in dry season was derived from fertilizer and sewage.
- Through soil layer, nitrate in surface was flushed into groundwater in wet season.
- Isotopes indicate that denitrification occurred in surface rather than groundwater.

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ABSTRACT

Water pollution in the form of nitrate nitrogen (NO_3^-–N) contamination is a major concern in most agricultural areas in the world. Concentrations and nitrogen and oxygen isotopic compositions of nitrate, as well as oxygen and deuterium isotopic compositions of surface and groundwater from a typical irrigated region in the North China Plain (NCP) collected from May to October in 2012 were analyzed to examine the major nitrate sources and transformations. Concentrations of NO_3^-–N ranged from 0.2 to 29.6 mg/L (mean of 11.2 mg/L) in surface water, and from 0.1 to 19.4 mg/L (mean of 2.8 mg/L) in groundwater. Approximately 46.7% of the surface water samples and 10% of the groundwater samples exceeded the World Health Organization (WHO) drinking water standard for NO_3^-–N. Surface water samples that exceeded the standard were collected mainly in the dry season (May and October), while groundwater samples that exceeded the standard were collected in the wet season (June). Overall, the highest nitrate levels were observed in surface water in May and in groundwater in June, indicating that fertilizer application, precipitation, and irrigation strongly influence the NO_3^-–N concentrations. Analyses of isotopic compositions suggest that the main sources of nitrate are nitrification of fertilizer and sewage in surface water, in contrast, mineralization of soil organic N and sewage is the groundwater sources during the dry season. When fertilizers are applied, nitrate will be transported by precipitation through the soil layers to the groundwater in the wet season (June). Denitrification only occurred in surface water in the wet season. Attempts should be made to minimize overuse of nitrogen fertilizers and to improve nitrogen use efficiency in irrigated agricultural regions.

1. Introduction

Nitrate contamination is a pervasive problem in China and all over the world (Erisman et al., 2013; Ju et al., 2009). The concentration of nitrate nitrogen (NO_3^-–N) in most rivers in populated regions reaches levels that are up to seven times higher than the maximum contaminant level (10 mg/L) allowed by the Global Environment Monitoring System database (He et al., 2011). High NO_3^-–N concentrations in drinking water increase the risk of diseases, such as certain types of cancers, methemoglobinemia, spontaneous abortions, diabetes, and thyroid disorders (Dan-Hassan et al., 2012). In addition to the health risk, once

Abbreviations: NO_3^-–N, nitrate nitrogen; NCP, North China Plain; WHO, World Health Organization; YCES, Yucheng Comprehensive Experiment Station; CAS, Chinese Academy of Sciences; EC, electrical conductivity; DO, dissolved oxygen; $\delta^{18}O$–H_2O, the isotopic compositions of oxygen in liquid water; δD, the isotopic compositions of deuterium in liquid water; SMOW, Standard Mean Ocean Water; GMWL, global meteoric water line; LMWL, local meteoric water line; MCL, the maximum contaminant levels.

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water resources are polluted by nitrate, recovery is associated with high costs related to a series of physical, chemical, and biological reactions used to decrease NO_3^-–N concentrations (Jiang et al., 2011).

A prerequisite for controlling and managing nitrate pollution is to identify sources of nitrate. Possible sources of nitrate contamination in water include agricultural N fertilizer, industrial wastewater discharges, urban domestic sewage, septic systems, human waste lagoons, animal feedlots, native soil organic matter, and atmospheric N deposition. It has been well established that nitrate dual isotope (^{15}N–NO_3^- and ^{18}O–NO_3^-) analysis is an effective approach for providing information on nitrate sources because of their distinct N and O isotopic compositions (Nestler et al., 2011). Nitrogen can be transformed through microbial processes, such as nitrification and denitrification, which are accompanied by isotopic fractionation (Kendall, 1998). In the denitrification process, NO_3^- is reduced to NOx or N_2 by bacteria, leaving the residual NO_3^- enriched in $\delta^{15}N$–NO_3^- and $\delta^{18}O$–NO_3^-. A crossplot of concentration and isotopic composition of NO_3^- can be used to evaluate mixing processes within hydrological systems (Kendall, 1998; Li et al., 2010b). No distinct positive or negative relationship between $\delta^{15}N$–NO_3^- or $\delta^{18}O$–NO_3^- vs. NO_3^- suggests that there is no simple mixing or only one biological process is responsible for the shifting of isotopic values. Nitrate originating from precipitation, synthetic nitrate fertilizer, or nitrification of reduced N fertilizer shows much lower $\delta^{15}N$ values (from −5‰ to +5‰) than from soil organic N (from 2‰ to +9‰), and manure and sewage (from 8‰ to +20‰). Although nitrate derived from precipitation, synthetic nitrate fertilizer, or produced by nitrification of reduced N compounds in fertilizer shows almost the same range of $\delta^{15}N$–NO_3^- values, they can be distinguished by their $\delta^{18}O$ values. Values of $\delta^{18}O$–NO_3^- in nitrate are usually between +20‰ and +70‰ in precipitation, between +17‰ and +25‰ in synthetic nitrate fertilizer, and lower than +15‰ in nitrification of reduced N fertilizer (Bateman and Kelly, 2007; Silva et al., 2002).

A growing number of studies have used dual isotopic analysis on nitrate to trace the main sources and transformations of nitrate from polluted rivers all over the world. For example, findings show that nitrification and urban sewage effluent are the major sources of nitrate in the Changjiang River in China (Li et al., 2010a); nitrification and denitrification contribute to nitrogen removal in the wetland area along a discontinuous tributary with slow water transport in the Tuul River (Itoh et al., 2011); the main nitrate source is atmospheric deposition or soil organic matter in the North Han River, but is manure or sewage in the South Han River in Korea (Lee et al., 2008); manure, fertilizer, and sewage are the major nitrate sources in a lowland agricultural catchment in eastern England (Wexler et al., 2009); the nitrate load in the Marano Lagoon in northeast Italy was derived not only from agriculture activities but also from other sources such as urban wastewaters, in situ nitrification, and atmospheric deposition (Saccon et al., 2013); and wastewater was an important nitrate source in urbanized streams in the Baltimore metropolitan area (Kaushal et al., 2011). However, there have only been a small number of studies on nitrate pollution in irrigated agricultural regions (Almasri and Kaluarachchi, 2004; C.Y. Zhang et al., 2013).

In agricultural regions, fertilizers and irrigation are the primary factors that contributed to increase world crop production. The use of fertilizers accounts for approximately 50% of the yield increase, and greater irrigation for another substantial part (Nellemann, 2009). China is the world's greatest producer and consumer of fertilizers using about 31% of the total amount of fertilizers used worldwide (Su et al., 2013). This large-scale use of chemical fertilizers has led to increasing water nitrate pollution. The North China Plain (NCP), which is the largest alluvial plain in China, provides about 61% and 31% of the nation's wheat and maize production, respectively (Zhao et al., 2013). Agricultural fertilization is a common practice in this region, which caused severe nitrate contamination of the local rivers and aquifers (Ju et al., 2009). In addition, irrigation is used to supplement seasonally deficient precipitation and to decrease soil salinity in the NCP (Liu and Luo, 2010). Approximately 75% of the agricultural land is irrigated, and it consumes 70% to 80% of the total water resources allocation (Chen et al., 2003). The City of Yucheng typifies the NCP's landscape, water, and soil resources (Jia et al., 2010). The nature and extent of agricultural development and industrialization are also typical of the wider NCP. The average NO_3^-–N concentration in surface water is 6.57 mg/L and in groundwater 10.23 mg/L (Chen et al., 2007; Chen, 2010). Nearly 39% of surface water samples (totally 31 samples) have nitrate levels in excess of the average value, and the percentage of groundwater samples with high levels are even greater in the Yellow River irrigation region (Wu et al., 2011). Chen et al. (2005) determined the distribution of nitrate pollution in various hydrogeological zones of the NCP's regional groundwater system. However, the sources and fate of nitrate in the NCP are still largely unknown. Also, advanced research into nitrate pollution due to changes in seasons in agricultural regions has been scant.

In this study, nitrate concentration, dual isotopic analysis of nitrate and water are used to (1) identify nitrate pollution in both surface and groundwater in irrigated agricultural regions, and (2) trace the main sources and transformations of nitrate in different seasons. This study provides useful information to evaluate the water quality and to promote a more sustainable water management in irrigated farming regions.

2. Materials and methods

2.1. Study region description

The NCP is located in the eastern part of China (35°00′–40°30′ N, 113°00′–119°30′ E) and represents a very important agricultural region, because of intense wheat, maize, cotton, and vegetable farming. The study region (36°41′13″–37°12′13″ N, 113°22′11″–116°45′00″ E) is in the central part of the NCP (Fig. 1) and hosts the Yucheng Comprehensive Experiment Station (YCES), Chinese Academy of Sciences (CAS). The study region has approximately 500,000 permanent residents, a total area of 990 km^2, and 529.27 km^2 of cultivated land. It lies within the Yellow River irrigation region and shows a warm temperate semi-humid climate with an average annual temperature of 13.1 °C. The annual precipitation is about 565.9 mm and much of the annual precipitation occurs between June and September (Fig. 2). The elevation above sea level ranges from 17.5 to 26.1 m. The dominant soil and rock types are clay soil and limestone, respectively. The geomorphology of the study area is characterized by a typical alluvial plain, whose slopes gradually increased from southwest to northeast.

Winter wheat and summer maize are the dominant crops, accounting for more than 70% of the planting area in the region. During the growth season, irrigation is usually required (Liu and Luo, 2010). Groundwater and surface water from local rivers and the Yellow River are supplied for farmland irrigation. The study area hosts 36 km of the main Yellow River irrigation channel. Diversion from the Yellow River provides about 70% of the local water resources. Other major rivers are the Tuhai, Zhaoniu, Wei, Danzhang, Shinv, Tuanjie, and Tuma Rivers (Fig. 1). The total amount of shallow groundwater resources is around 1.47×10^9 m^3. Approximately 80% of the groundwater resources are used for agriculture. Agricultural irrigation is carried out in May and November every year.

The depth of the shallow groundwater in the study area is between 3 and 20 m. Beneath the shallow aquifer a deeper groundwater layer exists in a depth of 40–70 m (Yang et al., 2009). The groundwater of both layers can be differentiated by their distinct hydrogen and oxygen isotope ratios. The shallow groundwater is characterized by rather heavy isotopes primarily from contemporary precipitation and diverted water, whereas the deeper groundwater is depleted with light isotopes from ancient precipitation. The residence time of shallow groundwater is between 20 and 50 years, whereas the age deeper groundwater is more than 8000 years (Yang et al., 2009). The infiltration rate and