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Nitrate in groundwater of China: Sources and driving forces

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ABSTRACT

Identifying the sources of reactive nitrogen (N) and quantifying their contributions to groundwater nitrate concentrations are critical to understanding the dynamics of groundwater nitrate contamination. Here we assessed groundwater nitrate contamination in China using literature analysis and N balance calculation in coupled human and natural systems. The source appointment via N balance was well validated by field data via literature analysis. Nitrate was detected in 96% of groundwater samples based on a common detection threshold of 0.2 mg N L^{-1}, and 28% of groundwater samples exceeded WHO's maximum contaminant level (10 mg N L^{-1}). Groundwater nitrate concentrations were the highest beneath industrial land (median: 34.6 mg N L^{-1}), followed by urban land (10.2 mg N L^{-1}), cropland (4.8 mg N L^{-1}), and rural human settlement (4.0 mg N L^{-1}), with the lowest found beneath natural land (0.8 mg N L^{-1}). During the period 1980–2008, total reactive N leakage to groundwater increased about 1.5 times, from 2.0 to 5.0 Tg N $year^{-1}$, in China. Despite that the contribution of cropland to the total amount of reactive N leakage to groundwater was reduced from 50 to 40% during the past three decades, cropland still was the single largest source, while the contribution from landfill rapidly increased from 10 to 34%. High reactive N leakage mainly occurred in relatively developed agricultural or urbanized regions with a large population. The amount of reactive N leakage to groundwater was mainly driven by anthropogenic factors (population, gross domestic product, urbanization rate and land use type). We constructed a high resolution map of reactive N source appointment and this could be the basis for future modeling of groundwater nitrate dynamics and for policy development on mitigation of groundwater contamination.

1. Introduction

Groundwater nitrate (NO_3^-) contamination is a threat to human health (Bryan and Loscalzo, 2011). About 5% of ingested nitrate is converted by bacteria in the digestive system to nitrite, which then forms *N*-nitrosamines and *N*-nitrosamides that damage DNA (Davidson et al., 2012). High nitrate concentration in drinking water can usually induce birth defects and cancers, which have been the subject of epidemiological studies (Johnson et al., 2010), particularly in rural agricultural areas where shallow groundwater is often used for domestic water supplies (Burow et al., 2010). Nitrate concentrations above the World Health Organization's (WHO's) maximum contaminant level (MCL, 10 mg N L^{-1}) are relatively common in some regions, especially in the emerging developing countries (Townsend et al., 2003; Burow et al., 2010).

Previous studies have identified the overuse of nitrogen (N) fertilizer to be one of the main sources for groundwater nitrate (Li et al., 2007; Kaushal et al., 2011). Meanwhile, groundwater nitrate can also be from other sources, such as sewer leakage and landfill leachate, which are of growing importance alongside urbanization (Mor et al., 2006; Gu et al., 2011a, 2012a). However, considerable uncertainty remains in our knowledge of the magnitude and spatiotemporal changes of groundwater nitrate concentrations owing to the many sources involved (Galloway et al., 2008; Burow et al., 2010). Therefore, understanding the sources and implementing source control are key issues on mitigating groundwater nitrate pollution.

Experimental sampling of groundwater on a large scale is usually lacking, and local scale experiments are difficult to be scaled up to regional and continental levels (Kaushal et al., 2011; Stigter et al., 2011). Thus, attaining a high resolution in the source appointment becomes an important approach in groundwater nitrate research. There are a large number of factors, such as

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climate (mean annual temperature, precipitation), human activities (urbanization, industrialization), economy and land use types, that affect the reactive N (Nr) leakage to groundwater (Birch et al., 2011; Gu et al., 2011a). Different Nr leaching sources may have different sensitivities to different driving factors. Understanding and quantifying human and natural factors that contribute to changes in groundwater nitrate concentrations are critical in prioritizing effective strategies for nitrate reduction from different sources.

China has been experiencing rapid industrialization and urbanization since the reform and opening up in the late 1970s. Currently, China consumes about 30% of the global anthropogenic N fixation on only 7% of the world's land base, and has been a hotspot of global N cycle (Townsend and Howarth, 2010; Cui et al., 2013). Serious groundwater nitrate pollution has occurred accompanying the tremendous socioeconomic development (Fu et al., 2007). China's national water quality assessment program has been monitoring groundwater quality in 182 main metropolitans and has found that the water quality of 57% (MEP, 2010) of all monitoring wells does not meet the clean groundwater standard (<20 mg N L^{-1} nitrate concentration, MEP, 1993). This has exposed residents to the risk of high nitrate concentration of groundwater in China (Liu and Diamond, 2008; Han et al., 2009a). However, currently, we do not know the overall patterns and dynamics of groundwater nitrate in China, especially in the rural area, and we do not fully understand how groundwater nitrate concentrations change with the rapid urbanization and economic development. In order to protect groundwater resources, the State Council of China has officially approved the ''National Groundwater Pollution Prevention Plan (NGPPP)'' on 24th August 2011. The NGPPP would invest about 6 billion US dollars to monitor groundwater pollution sources and remediate polluted groundwater before 2020. Thus, comprehensive quantification of the sources of Nr loading to groundwater in China is essential for the development of effective management practices for the most vulnerable areas.

The primary purposes of this study were to investigate the changes in the sources of groundwater nitrate on the spatiotemporal scale and the factors impact groundwater nitrate concentrations in China. To achieve these goals, we first conducted a literature analysis to understand the current status of groundwater nitrate pollution in China and the effect of land use type on groundwater nitrate concentration. Second, we carried out a source appointment analysis based on the coupled human and natural systems (CHANS) approach to identify and quantify specific sources of groundwater nitrate both on temporal (from 1980 to 2008) and spatial (provincial) scales. Third, we quantified the driving forces of changes in groundwater nitrate concentrations by considering natural and human factors. Finally, we estimated the spatial distribution of the sources at the county level, which was further used to compare with the literature analysis results of the current status of groundwater nitrate pollution, to assess the accuracy of source appointment analysis. This study produced a high resolution map of source appointment of groundwater nitrate concentrations in China that can be used for the modeling of groundwater nitrate dynamics in the future.

2. Methods

2.1. Literature analysis of groundwater nitrate

To understand the current status of groundwater nitrate concentrations in China, we reviewed more than 1000 published papers searched from Web of Science and China National Knowledge Infrastructure (CNKI) (2000–2012) and chose 108 of them for this analysis (Supplementary data Table S1) based on the following criteria: (i) publications in which groundwater nitrate concentration was determined; (ii) locations for the sampling sites were provided; (iii) the land use type, such as urban (non-industrial region), industrial, rural, cropland, or natural, of the sampling sites was clearly indicated. The urban area includes urban human settlements, commercial areas, parks, etc., but not including industrial regions. For the industrial area, samples are taken in factories or very close to the factories. For the rural area, samples usually are taken from villages. For cropland, samples are taken in cropland or very close to the cropland. The natural area generally includes natural forest, grassland, desert, etc.; (iv) the sampling date was after 1990. All data before 1990 were excluded since the intensity of human activities would be very different before and after 1990 in China and the data would be too old to be of use to represent the current groundwater nitrate status.

2.2. CHANS approach on source appointment

The CHANS approach covers and integrates all Nr fluxes and their interactions that can identify the specific sources of Nr to the environment (Alberti et al., 2011). Thus, the CHANS approach has recently been widely used on the studies of pollution source appointment (Werner and McNamara, 2007; Gu et al., 2011b, 2012a, b). The approach is useful in identifying the components and flows in crucial systems, and the linkages among subsystems, as well as analyzing the role of driving factors (Alberti et al., 2011). In this study, the CHANS is divided into four functional groups (Fig. S1; Table S2): processors, consumers, removers and life supporters, based on the mutual services among these groups, and each functional group includes several subsystems (14 subsystems in total). External N inputs first go through the processors (e.g., cropland, industry, etc.), and are then transferred to consumers for consumption, and on to removers (wastewater and garbage treatment) for Nr inactivation, and ultimately become an output from the system (Fig. S2, Gu et al., 2012b). The Nr from the processer, consumer and remover functional groups would leak to the life-supporter group (atmosphere, surface water and groundwater), contributing to the accumulation of Nr in that group (Gu et al., 2012a).

A mass balance approach was used to quantify the N fluxes for each subsystem in a CHANS of China (SI text) with over 6000 N flows (Gu et al., 2012b). Data were mainly derived from Chinese governmental statistical yearbooks and bulletins (e.g., NBS, 1981–2009) that supplied the best available data for the quantification of N fluxes and from published papers that were used for comparison (Table S3). On the basis of the N balance of the CHANS, we extracted all the Nr fluxes that were leaked from different subsystems to the groundwater. The specific sources of each Nr item were identified and quantified for different regions. We used the N Cycling Network Analyzer (NCNA) model to compile the dataset and to calculate all N fluxes (Min et al., 2011). This model can standardize the parameter collections for the N flux calculations, and automatically calculate the N fluxes and their relationships based on the mass balance approach (Fig. S3).

2.3. Estimates of Nr leakage at county level

Owing to the large amount of data required for source appointment using the CHANS approach, the spatial resolution of our calculation can only reach provincial level. Thus, regression models were used in this study to simulate the Nr loading to groundwater at the county level that could support a higher resolution assessment of the environmental and health effects. Although there are many sources of Nr (both natural and anthropogenic) that could potentially lead to the pollution of groundwater with nitrate, anthropogenic sources are the ones that most often cause the amount of nitrate to rise to a dangerous level