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Quantification of nitrate sources in groundwater using hydrochemical and dual isotopic data combined with a Bayesian mixing model

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ABSTRACT

To determine the contributions of various sources to nitrate loads in groundwater ($n = 103$) from three farmed rural sites in South Korea, we assessed the dual isotopic composition of nitrate, coupled with hydrochemical parameters. The measured isotopic values of nitrate varied widely, with 10th and 90th percentiles of 2.8‰ and 14.2‰ for $\delta^{15}N$, and 0.7‰ and 8.9‰ for $\delta^{18}O$, respectively and suggested that nitrification of anthropogenic N compounds is a predominant process of nitrate pollution. To overcome the known uncertainties of quantitative source apportionment for groundwater nitrate, arising from isotope fractionation during N transformations and the significant overlap in isotopic values of different sources, the combined hydrochemical and isotopic datasets were interpreted with orthogonal regression of a principal component analysis (PCA) and a Bayesian mixing model. The PCA projected the observed $\delta^{15}N_{NO_3}$ values onto a mixing subspace in the multivariate variability of the dataset, and the regression fits of the sample data were presumed to be conservative mixtures. This procedure also allowed for an assessment of the sample uncertainty, as influenced by natural nitrate contributions and denitrification. The Bayesian mixing model was used to estimate the probability distributions of the proportional contributions of three anthropogenic sources: chemical fertilizers, composted manure, and manure slurries. Nitrate is largely derived from chemical fertilizers with fractional contributions of 0.35–0.71, and organic fertilizers including composted manure with mixing fractions of 0.39–0.49. The relative contribution of nitrate from composted manure compared to chemical fertilizers increased with increasing nitrate concentrations, suggesting that composted manure significantly increases nitrate pollution and therefore its use should be carefully controlled to manage rural groundwater quality. This study also suggests that PCA and Bayesian isotope mixing models are effective for quantitative assessment of the sources of pollutants, such as nitrate.

1. Introduction

Groundwater is an important water resource, which is used for domestic consumption, including drinking water, as well as for irrigation in many rural communities. However, water quality has deteriorated worldwide, as a result of nitrate pollution from the agricultural application of inorganic and organic fertilizers, as well as from livestock manure (Harter et al., 2012 Dubrovsky et al., 2010 EEA, 2000 Mitsch et al., 1999). Groundwater quality data collected from the National Water-Quality Assessment (NAWQA) Program of US showed the following results: (1) the median values of nitrate concentrations of shallow groundwater (495 wells) increased from 3.2 to 3.4 mg/L between 1993 and 2003, (2) the proportion of shallow wells with nitrate concentrations greater than the Maximum Contaminant Level (44.3 mg/L NO_3) was 16–21%, and (3) agricultural fertilizers and animal wastes applied to croplands were the largest regional sources of groundwater nitrate, while other sources were locally relevant (Dubrovsky et al., 2010). Similarly, data for more than 13,000 groundwater bodies in EU countries showed that about 25% are in chemically "poor" status and the excessive levels of nitrate, due to the input and subsequent leaching of mineral and organic fertilizers, are the most frequent cause of "poor" groundwater status (EEA, 2000).

In South Korea, NIER (2012) recently reported a median groundwater nitrate-N concentration of 5.4 mg/L for 1500 wells (1032 domestic and 468 agricultural) in rural cropping-livestock

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farming areas, where 19.6% of samples exceeded the 10 mg/L allowable limit for drinking water. This nitrate level is much higher than average groundwater nitrate concentrations reported from other countries. For examples, the medial values of nitrate-N concentrations reported in US are 1.3 mg/L (Halberg and Keedny, 1993), 4.7 mg/L (Nolan et al., 1997) and 3.1 mg/L (Burow et al., 2010); and the average nitrate-N concentrations of groundwater in EU countries are generally above 2.26 mg/L corresponding to the threshold value of natural background level (EEA, 2000).

Nitrate pollution in groundwater is often attributed to poor management of nutrients in agricultural practices, such as the overuse of N-fertilizers. In particular, the overall N-use efficiency in the agricultural systems of South Korea is typically very low. Among the OECD countries, the use of inorganic N-fertilizers in the period 2002–2004 was the fifth highest, and the average surplus, representing the balance between N inputs and outputs, thereby indicating an increasing probability of groundwater pollution with nitrate, was highest with maximum and mean N surplus values of 240 and 74 kg/ha, respectively (OECD, 2008, 2012). The average application rate of N-fertilizers in South Korea is around 134 kg/ha/year (MIFFAF, 2012). In addition, livestock farming indirectly raises the nitrate level in groundwater, as further excess N is often added to agricultural fields in the form of large amounts of composted manure. Therefore, guidance for controlling these diffusive pollution sources and establishing an effective agricultural policy to reduce the amount of applied nitrogen is urgently needed, in order to prevent continued deterioration of groundwater quality in agricultural regions of South Korea.

To assess which nitrogen (N) sources are predominantly responsible for the nitrate contamination of surface water and groundwater, the dual isotopic composition of nitrate ($\delta^{15}N$ and $\delta^{18}O$) has proven a powerful tool (Deutsch et al., 2005 Fukada et al., 2004 Jin et al., 2012 Mattern et al., 2011 Seiler, 2005). Many authors have reported the dual isotopic ranges of diverse nitrate sources, and have determined the isotopic fractionations occurring during biogeochemical transformations of nitrogen, such as nitrification, volatilization, and denitrification (Böttcher et al., 1990 Clark and Fritz, 1997 DiSpirito and Hooper, 1986 Kendall, 1998 Kendall and Aravena, 2000 Kool et al., 2007 Mayer et al., 2001 Xue et al., 2009). However, despite its effectiveness, Xue et al. (2009) pointed out some limitations and uncertainties in the application of these isotopic analyses for nitrate source identification in water: (1) there is significant overlap in the isotopic ranges of multiple nitrate sources, and (2) there are complex fractionation effects during N transformation processes like denitrification. Therefore, attempts have been made to interpret the isotopic composition of nitrate within the context provided by additional information such as land use type, hydrochemical parameters, and the addition of tracers, such as boron isotopes, among others (Jin et al., 2012 Min et al., 2002 Spruill et al., 2002 Widory et al., 2004). Recently, Pastén-Zapata et al. (2014) demonstrated the usefulness of a multi-tracer approach using nitrate isotopes coupled with hydrochemical data (*esp*., halide ions) to differentiate various nitrate sources and processes. The interpretation of the complex datasets can be further improved using various statistical methods (Le Bot et al., 2011).

Another caveat in interpreting the observed isotopic compositions of nitrate in groundwater for the purposes of source apportionment is that nitrate is often derived from a mixture of potential sources during groundwater recharge (Böhlke, 2002), as hydrochemical mixing is a common process in many groundwater flow systems (Güler and Thyne, 2004). An alternative to using stable isotope mixing models to overcome the above-mentioned problems is the incorporation of Bayesian statistics. These statistical models estimate the confidence intervals for the contributions of a source to a mixture by taking into account

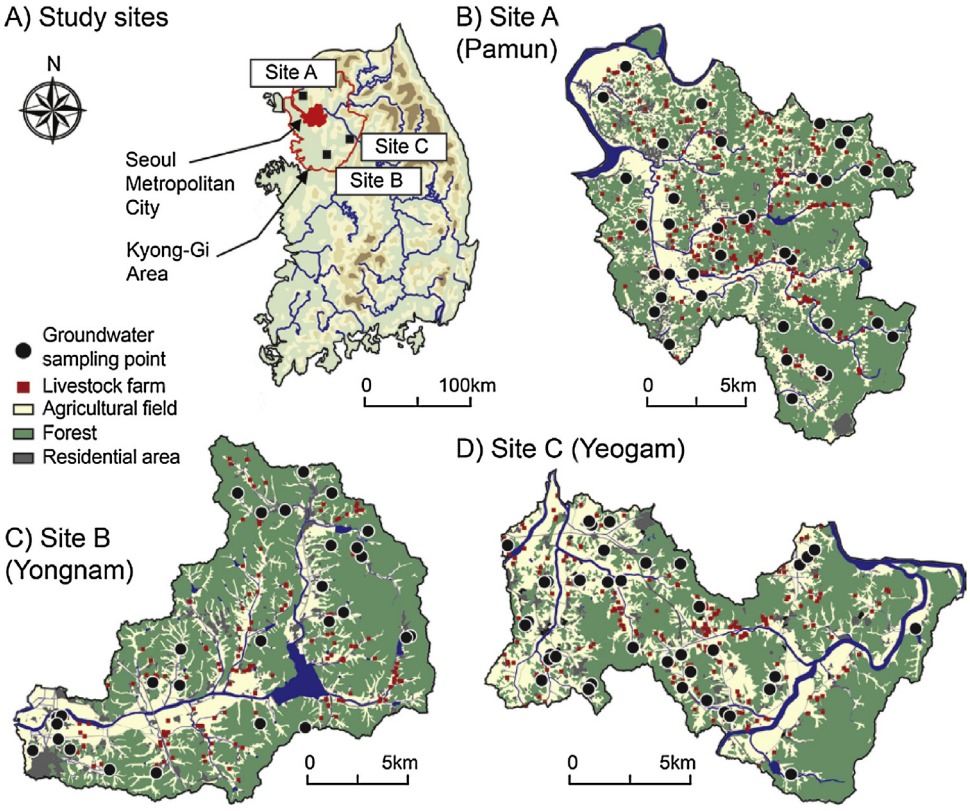

Fig. 1. Maps showing (A) locations of the three study sites (Pamun, Yongnam, and Yeogam) in Gyeonggi Province, Korea; and (B–D) groundwater sampling wells for hydrochemical and isotopic analysis within each area, respectively.