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Identifying the sources of nitrate contamination of groundwater in an agricultural area (Haean basin, Korea) using isotope and microbial community analyses

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HIGHLIGHTS

- Dual isotope analyses identified contaminant sources.
- Aquifer contamination was affected by land use.
- Microbial community in groundwater reflects land use.
- Approach is promising for managing water quality in agricultural areas.

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ABSTRACT

An integrated study based on hydrogeochemical, microbiological and dual isotopic approaches for nitrate and sulfate was conducted to elucidate sources and biogeochemical reactions governing groundwater contaminants in different seasons and under different land use in a basin of Korea. The land use in the study area is comprised of forests (58.0%), vegetable fields (27.6%), rice paddy fields (11.4%) and others (3.0%). The concentrations of NO_3–N and SO_4^{2-} in groundwater in vegetable fields were highest with 4.2–15.2 mg L^{-1} and 1.6–19.7 mg L^{-1} respectively, whereas under paddy fields NO_3–N concentrations ranged from 0 to 10.7 mg L^{-1} and sulfate concentrations were ~15 mg L^{-1}. Groundwater with high NO_3–N concentrations of >10 mg L^{-1} had $\delta^{15}N$–NO_3^- values ranging from 5.2 to 5.9‰ and $\delta^{18}O$ values of nitrate between 2.7 and 4.6‰ suggesting that the nitrate was mineralized from soil organic matter that was amended by fertilizer additions. Elevated concentrations of SO_4^{2-} with $\delta^{34}S$–SO_4^{2-} values between 1 and 6‰ in aquifers in vegetable fields indicated that a mixture of sulfate from atmospheric deposition, mineralization of soil organic matter and from synthetic fertilizers is the source of groundwater sulfate. Elevated $\delta^{18}O$–NO_3^- and $\delta^{18}O$–SO_4^{2-} values in samples collected from the paddy fields indicated that denitrification and bacterial sulfate reduction are actively occurring removing sulfate and nitrate from the groundwater. This was supported by high occurrences of denitrifying and sulfate reducing bacteria in groundwater of the paddy fields as evidenced by 16S rRNA pyrosequencing analysis. This study shows that dual isotope techniques combined with microbial data can be a powerful tool for identification of sources and microbial processes affecting NO_3^- and SO_4^{2-} in groundwater in areas with intensive agricultural land use.

1. Introduction

Contamination of groundwater with nitrate is a persistent problem especially in areas with intensive agricultural land use, and identifying the sources of nitrate is the first step to reducing groundwater pollution with nitrate. Nitrate in groundwater can be of natural or anthropogenic origin. Naturally occurring NO_3–N does usually not exceed concentrations of 3 mg L^{-1} in aquatic environments (Burkart and Kolpin, 1993). Higher concentrations of NO_3–N in groundwater are typically caused by anthropogenic activities including nitrogen compounds from synthetic fertilizers or manure used in agriculture, septic systems and other waste waters (McLay et al., 2001). In drinking water, concentration of NO_3–N in excess of 10 mg L^{-1} may result in blue baby syndrome in infants (methemoglobinemia) and may be a contributing factor for some types of cancer (Ward et al., 2005). In many agricultural regions, groundwater is often the major source of water both for drinking water and irrigation purposes. Groundwater contamination by nitrate derived from agricultural activities is a

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serious problem in many countries including Korea (Ju et al., 2006; Kaown et al., 2009; Koh et al., 2012). Understanding the sources of nitrate pollution in aquifers is a prerequisite for taking measures designed to reduce nitrate pollution of aquatic systems.

In many regions, nitrate contamination in groundwater is strongly correlated to land use and anthropogenic activities (McLay et al., 2001; Kaown et al., 2007). The increasing use of both animal waste products (e.g. manure) and inorganic fertilizers in agricultural areas complicates the identification of sources of nitrate contamination (Zhang et al., 1996). Isotopic studies of nitrate in groundwater are frequently undertaken because they often reveal information about sources of nitrogen contamination and processes such as mixing and denitrification (Kendall and Aravena, 2000). The isotopic composition of NO_3 can be used to discriminate between sources of nitrate, as nitrate originating from different sources has characteristic $\delta^{15}N$ and $\delta^{18}O$ values (Mayer et al., 2002; Kaown et al., 2009; Bronders et al., 2012; Gooddy et al., 2014; Pastén-Zapata et al., 2014: Zhang et al., 2014). In addition, the process of denitrification preferentially metabolizes the light isotopes ^{14}N and ^{16}O thereby enriching ^{15}N and ^{18}O in the remaining nitrate (Strebel et al., 1990). This leads to characteristic trends of increasing $\delta^{15}N$ and $\delta^{18}O$ values as nitrate concentrations decrease suggesting that denitrification occurs. Whether this process is coupled with oxidation of organic matter or with pyrite oxidation can be further revealed by isotope analyses on sulfate, since sulfide oxidation typically yields significantly increased concentrations of sulfate in the aquifer with low $\delta^{34}S$ and $\delta^{18}O$ values of the sulfate (McCallum et al., 2008). Therefore, the dual isotope approach for nitrate and sulfate ($\delta^{15}N$–NO_3^-, $\delta^{18}O$–NO_3^-, $\delta^{34}S$–SO_4^{2-}, and $\delta^{18}O$–SO_4^{2-}) is often effective in identifying the contaminant sources and the processes leading to nitrate and sulfate contamination of aquifers (Kaown et al., 2009; Otero et al., 2009; Hosono et al., 2011; Urresti-Estala et al., 2015). For example, hydrogeological and multi-isotopic methods were successfully used to assess the fate of groundwater nitrate in Osona, Spain (Otero et al., 2009), to elucidate complex pollution causes in the urban shallow groundwater in Taipei, Taiwan (Hosono et al., 2011), and to assess the causes of rural groundwater contamination in Alberta, Canada (McCallum et al., 2008).

Over the past several decades, denitrification and bacterial sulfate reduction in groundwater have become recognized as important redox processes affecting the groundwater environment (e.g. Mariotti et al., 1988). Combining bio-molecular methods and isotope analysis with geochemical approaches has yielded new insights into the complexity of these redox processes (Brunner and Bernasconi, 2005). The comparison of bacterial communities with isotope data has the potential to provide further insight into species and sources of bacteria that potentially assist in controlling groundwater pollution with nitrate and sulfate dependent on the land use patterns.

The groundwater of the study area in the Haean Basin of Korea has been contaminated by NO_3–N and SO_4^{2-} due to intensive agricultural activities accompanied by the widespread use of large quantities of organic and inorganic fertilizers. The spatial and temporal distributions of NO_3–N and SO_4^{2-} in the shallow groundwater show a wide variation according to the land use, cycle of applied fertilizers, and heterogeneity of the aquifer (Kaown et al., 2009). Since groundwater is one of the main water resources in the area, it is of crucial importance to prevent further contamination of groundwater. Therefore, it is desirable to identify the sources of groundwater contaminants and to identify the processes that may assist in their natural attenuation for efficient management of water resources.

The objective of this study was to determine sources and processes affecting nitrate and sulfate in groundwater in an intensive agricultural area over the heterogeneous aquifer of the Haean basin, South Korea. We employed the dual-isotopic approach for nitrate and sulfate combined with hydrogeochemical data and bio-molecular methods with meta-genomic analysis to characterize source and processes affecting NO_3^- and SO_4^{2-} in groundwater. The relationships between dual isotope data, microbial communities and in situ biodegradation of NO_3^- and SO_4^{2-} and their dependence on land use patterns were evaluated to assess the potential contribution of bacterial communities to the removal of NO_3^- and SO_4^{2-} from the aquifer. The goal was to provide new information for groundwater quality management (e.g. nitrate and sulfate contaminants in groundwater) in an intensive agricultural area to assist in the development of criteria for agricultural groundwater quality management planning and legislation (KME, 2015) by the Korea Ministry of Environment. This study should help with placing the water quality effects in perspective with other factors affecting the hydro-ecosystem with the ultimate goal of obtaining a sustainable clean water supply not only for irrigation but also for drinking water purposes.

2. Study area

2.1. Site description

This study was conducted in the Haean basin (128°5'–128°11'E; 38°15'–38°20'N) in Yanggu Country, Gangwon Province, in the north-eastern part of Korea (Fig. 1a). The size of the basin is approximately 64 km^2. The east–west length of the basin is 6.6 km and the north–south length is 11.95 km. The geology of the study area is characterized by Jurassic igneous rocks intruding into composite metamorphic rocks composed of mica schists, biotite-feldspar gneiss and quartzite. The basin is surrounded by high mountains (Daeam, Deawoo, Dosol and Gachilbong) reaching elevations of up to 1320 m above sea level (a.s.l.). The research area is a bowl shaped mountainous basin with a range in altitude from 339 m in the center to 1320 m a.s.l. on the mountainous fringes (Fig. 1b) that have an average slope of 28% and a maximum slope of 84% (Kettering et al., 2012). The basin was formed by differential erosion (Lee, 2009; Kim et al., 2013, 2014) since the outer parts of the basin are predominantly composed of harder weathering-resistant metamorphic rocks, whereas the interior of the basin is predominantly composed of granite (Kim and Park, 1967), which is more vulnerable to weathering. Much of the granite near the surface has weathered to saprolite and is overlain by soils derived from these bedrocks. Groundwater is recharged throughout the watershed with elevated recharge in the mountain area and flows generally towards the bottom of the basin that is drained by three main streams (Seonghwang, Dosol, Mandae) with several tributaries. These streams leave the basin at the eastern border of the study area, where they eventually converge with the Soyang River. This river water serves as a major source of drinking water supply for the metropolitan city of Seoul. Therefore, to ensure the supply of clean drinking water from the Haean catchment it is of critical importance to control agricultural pollution of groundwater, potentially via regulation of fertilizer usage.

The climate in the study area is characterized by distinct rainy and dry seasons. Mean annual precipitation (monitored from 2003 to 2012) was 1372 mm (Korea Metrological Agency, 2014). High precipitation occurs generally between June and August with 64% of the annual rainfall and December to February with 29% of the annual snowfall, respectively.

The aquifer of this area consists of weathered granite overlain by alluvial deposits of up to 10 m thickness (Lee, 2009). The alluvial deposits are primarily composed of sand, gravel, and scree. The hydraulic conductivity for estimation of flow velocity, determined by slug and pumping tests, was found to range from 4.94×10^{-5} cm s^{-1} (well Y21) to up to 1.0×10^{-3} cm s^{-1} (wells 23, and 33) in the unconfined aquifer suggesting groundwater velocities in the aquifer from < 50 cm/year to >1 m/year in the flat lower portions of the basin. The total amount of groundwater abstracted for domestic and agricultural usage is on average 2000 to 4000 m^3 day^{-1} in the growing season. The transmissivity of the aquifer assessed at a groundwater well located at 500 m (a.s.l.) was 2.6–3.0 m^2 day^{-1}. According to drilling records, soils are up to 2 m thick, underlain by 3–5 m of sand and gravel, 4–5 m of scree, and 5–10 m of weathered bedrock. Groundwater is