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Origin and fate of nitrate runoff in an agricultural catchment: Haean, South Korea – Comparison of two extremely different monsoon seasons

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HIGHLIGHTS

- Heavy monsoon rainfall severely increased river nitrate discharge.
- Majority of nitrate runoff underwent microbial nitrification.
- After heavy monsoon rainfall groundwater nitrate contributed to river discharge.
- Groundwater nitrate partially underwent microbial denitrification
- Atmospheric nitrate deposition and direct nitrate fertilizer leaching had only minor relevance.

GRAPHICAL ABSTRACT

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ABSTRACT

The monsoon season in South Korea has great influences on biogeochemical and hydrological processes in the entire country, but is specifically of concern in the Soyang lake watershed, the main drinking water reservoir for the 20-million-people metropolis Seoul. Therefore, water quality and nitrate concentration control in Lake Soyang is of high public priority. The Haean catchment is the most prominent agriculture-dominated sub-catchment of the Soyang lake watershed. It is a complex terrain influenced by extreme rain events and non-point nitrate sources. In this investigation we used input-output calculations and a stable isotope approach to quantify and determinate the origin of nitrate inputs into the rivers that later flow into the lake. During pre-monsoon and monsoon seasons in 2013 and 2014 we measured daily rainfall and river water discharge within the Haean catchment and collected rain, river water and groundwater samples in order to analyze nitrate concentrations and nitrate nitrogen and oxygen isotope abundances. Furthermore, we collected nitrogen fertilizers as applied in the catchment. Heavy monsoon events, as in 2013, were the most pronounced drivers of nitrate leaching being responsible for >80% of the nitrate output in the river runoff. On the other hand, an almost missing summer monsoon in 2014 drove the nitrate runoff in a different manner, being responsible for only 0.4% of the total nitrate nitrogen river discharge in the previous year. Results of nitrate nitrogen and oxygen isotope abundance analyses suggest soil microbial nitrification as the most important contributor to the nitrate in the river runoff. In addition, nitrate from groundwater partially affected by microbial denitrification contributed to the nitrate in the runoff due to river-aquifer exchange fluxes during the monsoon season. Direct leaching of nitrate from mineral fertilizers and atmospheric nitrate deposition were obviously only minor contributors to the nitrate in the runoff.

1. Introduction

Nitrate leaching from agricultural land is considered as a hazardous source of pollution of surface water and groundwater systems (Zotarelli

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et al., 2007). Specifically, anthropogenic nitrogen fertilizer applications on agricultural land frequently lead to nitrate exports from rooted soil horizons to aquatic ecosystems, like rivers, natural lakes and drinking water reservoirs (Cheong et al., 2012; Kraft and Stites, 2003; Lee et al., 2008; Oelmann et al., 2007; Oren et al., 2004). Nitrate export into aquatic systems causes eutrophication and acidification accompanied by deficiencies of dissolved oxygen and subsequent loss of animal and plant species (Camargo and Alonso, 2007). Drinking water with concentrations above 11 mg L^{-1} of N_{NO3}^{-} (Cheong et al., 2012; Kim et al., 2015; Ward et al., 2005; World Health Organization, 2011) causes health problems for humans, as the well-known methaemoglobinaemia or blue baby syndrome as well as different types of cancer in adults, especially in the digestive tract (Powlson et al., 2008).

Soyang lake watershed in South Korea is the major drinking water reservoir for the 20-million-people metropolis Seoul (Kim et al., 2000; Park et al., 2010). Therefore, control of water quality, especially nitrate concentrations in Lake Soyang, is of high public priority. The identification of nitrate sources and total nitrate exports in the Soyang lake watershed is a major concern for decision makers in the entire country. The watershed has a complex terrain with different types of land use, including patches of semi-natural silviculture and intensive agricultural management specifically in the Haean basin (Kim, 2016). In addition, high altitudinal gradients and monsoon-driven extreme rainfall variations cause a high risk of nitrate leaching and soil erosion (Arnhold et al., 2014; Park et al., 2010). These characteristics entail complex consequences and impacts in the environment that have to be considered for any improvement of water quality predictions in the region.

A common practice in the Haean basin is the addition of sandy soil to the top layer of agricultural fields to compensate for soil loss by erosion during monsoon seasons (Berger, 2012). Also heavy mineral nitrogen fertilizer applications are used to compensate for soil erosion loss. Thus, a circle system difficult to break is created, in which high nitrogen fertilizer applications together with heavy monsoon rainfalls and sandy soils make this basin a potential hazard in terms of nitrate losses. The situation may become even more hazardous when considering changes in the monsoon regime with general global climate change. Ashfaq et al. (2009) and Cruz et al. (2012) suggested a suppression of summer precipitation, a delay in monsoon onset, an increase in the occurrence of monsoon break periods, as well as variations of total rain distribution in the east Asian summer monsoon, due to the small scale regional circulations which are more vulnerable to climate change (Rajeevan et al., 2008). In contrast, Wang et al. (2006) found that regardless of the large amplitude of year-to-year variations, the total summer monsoon rainfall has increased by approximately 7% per century.

In areas with only one recognizable nitrate source the calculation of total nitrate exports might be sufficient for an effective decision making. However, in areas with complex terrain, extreme weather events and non-point nitrate sources, like in the Haean basin, a simple nitrate export mass balance may not be sufficient to elucidate in a mechanistic manner the origin of nitrate exports. Additional information on biogeochemical key processes in the nitrogen cycle is required. Stable isotope natural abundance of nitrate is an ideally suited tool to add source and process information to nitrate input-output calculations on a catchment level.

Stable isotope abundance of nitrate has frequently been used to identify nitrate origins. Unfortunately $\delta^{15}N_{NO3}^{-}$ from different origins often shows overlapping ranges (Durka et al., 1994; Gormly and Spalding, 1979; Koh et al., 2010; Kreitler, 1979; Mayer et al., 2002, 2001). Processes such as microbial nitrification or denitrification are hard to identify using only $\delta^{15}N_{NO3}^{-}$ without additional support, since significant nitrogen fractionation occurs during these microbial processes (Wassenaar, 1995). On the other hand, high fractionation during these microbial processes affects simultaneously oxygen isotope abundance (Koh et al., 2010). For example nitrate produced during microbial nitrification contains two-thirds of its oxygen from soil water and one third of its oxygen from atmospheric oxygen (Andersson and Hooper, 1983; Durka et al., 1994; Kendall, 1998; Ohte et al., 2004; Wassenaar, 1995). Thus, nitrate generated by microbial nitrification has distinct oxygen isotope ratios particularly different from atmospheric nitrate deposition, denitrification and fertilizers. Therefore, additional measurement of $\delta^{18}O_{NO3}^{-}$ is required for a more precise classification of nitrate origins (Amberger and Schmidt, 1987; Aravena and Robertson, 1998; Böttcher et al., 1990; Bräuer and Strauch, 2000; Durka et al., 1994; Revesz et al., 1997; Silva et al., 2000) particularly in agricultural areas where nitrate based fertilizers are used (Wassenaar, 1995).

Another example is microbial denitrification, which causes enrichment in $\delta^{15}N$ and $\delta^{18}O$ in the remaining nitrate and simultaneously decreasing nitrate concentration (Mariotti et al., 1982, 1981). During denitrification $\delta^{15}N_{NO3}^{-}$ increases about twice as fast as $\delta^{18}O_{NO3}^{-}$ especially under closed system conditions (Melorose et al., 2015).

Thus, the dual isotope approach analyzing $\delta^{15}N_{NO3}^{-}$ and $\delta^{18}O_{NO3}^{-}$ is suited to separate nitrate that underwent nitrification and denitrification from each other and from other nitrate sources.

For example, Deutsch (2006) successfully identify atmospheric deposition as one of three sources in a riverine zone. Einsiedl and Mayer (2006) identified proportional contributions of nitrate sources including nitrification, synthetic fertilizers and atmospheric deposition in groundwater in Germany.

In this study we compared nitrate inputs and outputs and underlying biogeochemical nitrate transformation processes in the Haean catchment for two years extremely different in their summer rainfall patterns. In 2013 a dry pre-monsoon season was followed by a monsoon season with rainfall amounts equal or above the eleven-years average (Kim et al., 2007). In contrast, in 2014 a monsoon season almost completely failed leading to rainfall amounts substantially below the eleven-year average (Kim et al., 2007). We used the extreme differences in summer precipitation between 2013 and 2014 to develop scenarios for nitrate exports from agricultural catchments in summer monsoon climate regions under conditions as predicted by global climate change scenarios.

2. Materials and methods

2.1. Study site and land use

The field portion of this research was conducted in the Haean-myun basin located in Yanggu–County, Gangwon Province, in the northeastern part of South Korea (128° 5′ to 128° 11′ E, 38° 13′ to 38° 20′ N). The punchbowl shaped basin is part of the Soyang lake watershed, which is the largest water reservoir in the country (Kim et al., 2000), and it is the main source of drinking water for the 20-million-people metropolis Seoul (Fig. 1). The Haean basin has a total area of 64 km^2. It is the major farming territory of the entire watershed (Park et al., 2010) with about 30% area under agricultural land use (22% dry land fields and 8% rice paddies). 58% of the area are forested mountains and 12% are residential and semi-natural areas including grassland, field margins, riparian areas, channels, and farm roads (Arnhold et al., 2013). The topography of the area is complex with different hillslopes and flow directions (Arnhold et al., 2014). It has different altitudinal gradients characterized by flat areas and steep slopes in the mountain forested ridges (Arnhold et al., 2014; Park et al., 2010). The altitudinal elevation gradient reaches from 340 m above sea level (asl) at Mandae River near the catchment outlet up to 1320 m asl in the surrounding mountain forests.

The maximum and minimum temperatures in the Haean basin per year span from −27 °C in winter to +33 °C in summer. The mean annual air temperature is 8.7 °C, and the annual precipitation based on 13 years weather station records in the Haean basin is 1658 mm, (Maharjan, 2015). Almost 90% of the annual precipitation occurs within the cropping season from April to October (Kettering et al., 2012). The monsoon season occurs in July, August, and September with great influence on the biogeochemical and hydrological processes as it represents