



## Tracing freshwater nitrate sources in pre-alpine groundwater catchments using environmental tracers



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### SUMMARY

Groundwater is one of the main resources for drinking water. Its quality is still threatened by the widespread contaminant nitrate ( $\text{NO}_3^-$ ). In order to manage groundwater resources in a sustainable manner, we need to find options of lowering nitrate input. Particularly, a comprehensive knowledge of nitrate sources is required in areas which are important current and future drinking water reservoirs such as pre-alpine aquifers covered with permanent grassland. The objective of the present study was to identify major sources of nitrate in groundwater with low mean nitrate concentrations ( $8 \pm 2 \text{ mg/L}$ ). To achieve the objective, we used environmental tracer approaches in four pre-alpine groundwater catchments. The stable isotope composition and tritium content of water were used to study the hydrogeology and transit times. Furthermore, nitrate stable isotope methods were applied to trace nitrogen from its sources to groundwater. The results of the nitrate isotope analysis showed that groundwater nitrate was derived from nitrification of a variety of ammonium sources such as atmospheric deposition, mineral and organic fertilizers and soil organic matter. A direct influence of mineral fertilizer, atmospheric deposition and sewage was excluded. Since temporal variation in stable isotopes of nitrate were detected only in surface water and locally at one groundwater monitoring well, aquifers appeared to be well mixed and influenced by a continuous nitrate input mainly from soil derived nitrogen. Hydrogeological analysis supported that the investigated aquifers were less vulnerable to rapid impacts due to long average transit times, ranging from 5 to 21 years. Our study revealed the importance of combining environmental tracer approaches and a comprehensive sampling campaign (local sources of nitrate, soil water, river water, and groundwater) to identify the nitrate sources in groundwater and its vulnerability. In future, the achieved results will help develop targeted strategies for a sustainable groundwater management focusing more on soil nitrogen storage.

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### 1. Introduction

Groundwater is the dominant resource for drinking water in several European countries like Austria, France, Germany and Italy (Hulsmann, 2011); however its quality is threatened by contamination with nitrate ( $\text{NO}_3^-$ ). Nitrate contamination of groundwater causes negative effects to human health, since especially infants are endangered by Methemoglobinemia (Fan and Steinberg, 1996). In the last years (2008–2011), 14.4% of groundwater sites selected for long-term monitoring in the European Union exceeded a concentration of 50 mg/L nitrate concentration and an additional 5.9% were in the 40–50 mg/L range (EU-Commission, 2013). The more groundwater catchments fail to

meet drinking water standards, the more pressure is put on other aquifers as current and future drinking water reservoirs. Therefore, action has to be taken now to keep the good chemical status of aquifers and to ensure these aquifers do not exceed drinking water limits for nitrate, which is also in the scope of the Water Framework Directive (WFD, 2000). One important measure for this is the identification of nitrate sources. To date, most of the studies concerning nitrate source identification were carried out for already contaminated groundwater catchments containing  $>50 \text{ mg/L NO}_3^-$  (Aravena et al., 1993; Diédhiou et al., 2011; Hosono et al., 2013; Puig et al., 2013). However, existing studies fail to investigate sources of nitrate in aquifers currently having a good chemical status, which is the scope of the present study. Such aquifers must be managed in a sustainable way to guarantee long-term protection from nitrate contamination.

Nitrate in groundwater often originates from a mix of several sources, mainly derived from agricultural activity (mineral and

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organic fertilizers) and atmospheric deposition (Erisman et al., 2011; Stoate et al., 2001; Strelbel et al., 1989). In order to safeguard our groundwater resources from contamination, there is a need to identify and minimize potential sources by establishing appropriate management plans. This is of particular importance in areas dominated by agriculture and thus expected to intensively contribute to future drinking water supply, such as pre-alpine areas or similar aquifers with high water yield. Since potential sources of nitrogen input (e.g. mineral fertilizer, sewage, atmospheric deposition) have distinct nitrate stable isotope signatures ( $\delta^{15}\text{N}_{(\text{NO}_3)}$ ,  $\delta^{18}\text{O}_{(\text{NO}_3)}$ ) (Kendall and McDonnell, 1998), they can be further traced in the water cycle (e.g. (Aravena et al., 1993; Mayer et al., 2002; Nisi et al., 2013; Wassenaar, 1995). However, identification of nitrate origin is challenged if (i) multiple potential sources lead to a mixed isotopic composition of the product (Kaown et al., 2009), (ii) biogeochemical processes alter the initial isotope value (Moore et al., 2006) or (iii) hydrological conditions like mixing of water with different isotopic composition occur (Widory et al., 2004). To distinguish between nitrate sources with similar isotope ratios like  $\delta^{15}\text{N}_{(\text{NO}_3)}$  in organic fertilizer and sewage, additional tracers have to be considered like food additives and chloride concentration (Fenech et al., 2012). Biogeochemical processes, such as mineralization and denitrification, lead to the fractionation of the initial composition of stable isotopes of nitrate. For example, during denitrification the  $\delta^{15}\text{N}:\delta^{18}\text{O}$  ratio of the residual nitrate evolves along a slope of approximately 1:2, which is frequently used as evidence that denitrification has taken place (Aravena and Robertson, 1998; Böttcher et al., 1990; Sacchi et al., 2013). Since the described biogeochemical processes mainly occur in soil, soil acts as reactor for nitrogen transformation and needs to be included into nitrate-source studies. Both water flow and transport conditions can influence the isotope composition of nitrate in groundwater, due to the mixing of different sources (e.g., due to different flow paths, dispersion) and transformation processes along the flow paths (e.g. caused by changes in redox conditions). Thus, the local hydrogeology needs to be part of any investigation tracing nitrate origin in groundwater. Considering the time delay between infiltration of nitrate pollution and its appearance in groundwater (Diédhiou et al., 2011; Hinkle et al., 2007), groundwater studies struggle with an appropriate temporal assignment of nitrate contamination. Vice versa, reducing nitrate input affects the groundwater quality only after a certain time lag due to nitrogen turnover processes in soil and the mean transit time of groundwater recharge (Sebilo et al., 2013). Estimating transit time of groundwater combined with the identification of nitrate sources provides information about the infiltration history (Koh et al., 2010; Moore et al., 2006).

Both nitrate leaching (Di and Cameron, 2002) and sources of nitrate (Diédhiou et al., 2011; Koh et al., 2010; Pastén-Zapata et al., 2014) are strongly affected by land use. For less contaminated aquifers it was shown that the nitrate present in groundwater below residential areas originated from domestic wastewater (Koh et al., 2010; Pastén-Zapata et al., 2014) and that the nitrate in groundwater below vegetable fields and orchards originated from manure and nitrification of soil organic matter (Kaown et al., 2009). Considering that nitrate leaching is lower under permanent grassland compared to other land use (Di and Cameron, 2002),  $\delta^{15}\text{N}_{(\text{NO}_3)}/\delta^{18}\text{O}_{(\text{NO}_3)}$ -studies on groundwater catchments covered with permanent grassland are rare. Soil zone studies were conducted to distinguish between different sources of nitrate under legume monocultures (Oelmann et al., 2007) and permanent grassland (Granger et al., 2008; Minet et al., 2012). Stable isotopes of nitrate in analyzed soil water made it possible to distinguish between atmospheric deposition and mineralization of leguminous and non-leguminous soil organic matter as sources of nitrate (Oelmann et al., 2007). In contrast, the isotopic

composition of nitrate in soil water under grassland barely mirrored the isotope composition of corresponding N applications (cattle slurry, atmospheric deposition, mineral fertilizer, dairy wastewater), but matched with nitrified soil organic nitrogen (Granger et al., 2008; Minet et al., 2012). Since the mentioned studies investigated soil water, the question arises whether nitrate sources can be identified at catchment scale covered with permanent grassland, which is presumed to be the most appropriate land use for water protection areas besides forest.

We need to study in more detail nitrate sources in aquifers which are important as current and future drinking water reservoirs. In Europe, such aquifers are located in pre-alpine areas and are of importance due to their high water yield, good chemical status and high proportion of grassland. Therefore, the objective of the present study was to identify major sources of nitrate in oligotrophic pre-alpine aquifers. The study was performed in four pre-alpine groundwater catchments used for drinking water purposes to examine the potential nitrate contamination. Achieving the objective, different isotopic and environmental tracers were used to understand the local hydrogeology and the fate of nitrate and related transformation processes. Spatial and temporal distribution of nitrate concentrations and sources in pre-alpine groundwater systems were identified. The findings of this study are necessary to achieve sustainable use of groundwater and allow targeted strategies to better manage drinking water production.

## 2. Study area and methods

### 2.1. Study area

The observation site is located in Germany, covers an area of 126 km<sup>2</sup>, and the elevation ranges from 602 to 864 m a.s.l. The temperate climate in the study area is characterized by the long-term annual mean precipitation, ranging from 1500 to 2000 mm (1961–1990) and the air temperature of 6.9 °C (DWD, 2011). The local annual mean groundwater recharge was calculated from precipitation data from 1991 to 2011 (633–989 mm year<sup>-1</sup>, T. Dittmann, project thesis, data unpublished) using the FAO guideline (Allen et al., 1998).

The investigation area contains four unconfined quaternary porous aquifers (aquifers A, B, C, D) (Fig. 1a). They were developed by glacial abrasion of tertiary layers and the erosion caused by melting water, cutting into the tertiary relief as reported in the geological map (Grottenthaler et al., 1985). Aquifers B and D were escarped due to erosion processes of the river R1, resulting in rich outcrop springs. The lower boundary of all four aquifers is defined by impermeable tertiary sediments and its contour lines are given in Fig. 1a. Note that the south-west wards incoming aquifer splits into aquifer B and aquifer A. Quaternary sediments originated from alpine limestone fillings cover the tertiary relief and reach a total thickness of up to 80 m; the thickness of the actual groundwater bodies varies (5–20 m). The quaternary sediments are a mix of sands, gravels and cobbles (alluvial and glacial origin), resulting in a heterogeneous permeable matrix with a saturated hydraulic conductivity of 10<sup>-3</sup> m/s to 10<sup>-4</sup> m/s (Grottenthaler et al., 1985). The total catchment areas of the aquifers used for municipal and local drinking water supply are mainly unknown, but expand further south-west wards. The location of production and monitoring wells involved in this study is shown in Fig. 1a. Screen intervals for monitoring wells vary between 8 and 20 m covering the entire extent of the aquifer. Production wells are installed horizontally in the middle of the aquifers. Due to intense production rates and high hydraulic conductivities, the pumped water is assumed to be representative of the entire aquifer. Information about flow direction and delineation of the aquifers was provided by local

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