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Evidence for denitrification regulated by pyrite oxidation in a heterogeneous porous groundwater system

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ABSTRACT

Denitrification is an important natural attenuation process that has been observed in many fissured and porous aquifers. However, an important factor limiting denitrification in aquatic systems is the microbial availability of electron donors. Pyrite as the most abundant sulfide mineral in nature represents one of the potential electron sources for denitrifiers to reduce nitrate, but the reaction mechanisms coupling denitrification processes to pyrite oxidation are still questionable. We utilized hydrochemical data and stable isotopes of nitrate and sulfate in groundwater, isotope ratios of sulfur compounds in aquifer sediments and tritium based groundwater dating for assessing denitrification processes in a pyrite-bearing porous groundwater system. The oxic part of the aquifer with mean water transit times of approximately 60 years was characterized by nitrate concentrations of around 15 mg/l and $\delta^{15}N$ values were similar to those typical for nitrification. In contrast, in the anoxic part with mean water transit times of up to 100 years, low nitrate concentrations accompanied by elevated $\delta^{15}N$ values were observed. Furthermore, isotope data of groundwater sulfate and sulfur compounds in the aquifer sediment suggest that pyrite oxidation is the dominant source of sulfate in the aquifer. The trend of increasing $\delta^{15}N$ values and decreasing nitrate concentrations in concert with depleted $\delta^{34}S$ values of groundwater sulfate similar to $\delta^{34}S$ values of pyrite, FeS_2, suggests that denitrification is coupled to pyrite oxidation, particularly when water mean transit time is elevated.

1. Introduction

Nitrate is one of the world's most common pollutants in terrestrial ecosystems (Trudell et al., 1986). During the last 50 years, human activities have dramatically increased inputs of nitrogen to groundwater (Puckett et al., 2002) representing one of the most important drinking water resources. Although NO_3^- is of minor toxicity, secondary reaction products in human metabolism such as NO_2^- and nitrosamines can affect human health ("blue baby" syndrome) or might raise the risk of cancer (WHO, 1998).

NO_3^- in groundwater can be derived from natural and anthropogenic sources. In catchments with mainly agricultural land use NO_3^- is usually derived from N-fertilizers and manure, and concentrations in groundwater in excess of the drinking water guideline of 50 mg/l NO_3^- are observed (WHO, 1998). Effective elimination of NO_3^- from groundwater can only be achieved by anaerobic ammonium oxidation (anammox) and denitrification. The latter is the microbially induced reduction of NO_3^- or NO_2^- to the gaseous products N_2O and N_2 (Korom, 1992).

Sources and processes affecting groundwater NO_3^- can be characterized by means of its isotopic composition ($\delta^{15}N$, $\delta^{18}O$) which has been successfully used in numerous field studies (Amberger and Schmidt, 1987; Wassenaar, 1995; Mengis et al., 1999; Katz et al., 2001; Panno et al., 2001; Beller et al., 2004; Einsiedl and Mayer, 2006). During denitrification, microorganisms prefer the lighter isotopes ^{14}N and ^{16}O leaving the remaining nitrate progressively enriched in ^{15}N and ^{18}O. Moreover, in groundwater systems the isotopic enrichment of ^{18}O and ^{15}N results in a typical ratio of 1:2. Therefore, in a plot of $\delta^{18}O$ against $\delta^{15}N$, denitrification yields a linear trend line with a slope of around 0.5 (Böttcher et al., 1990; Aravena and Robertson, 1998; Cey et al., 1999; Mengis et al., 1999; Lehmann et al., 2003).

So far, numerous studies have been performed showing the occurrence of denitrification in groundwater by means of hydrochemical and isotopic data. Most of the studies focused on the denitrification potential of riparian buffer zones, which have been suggested to provide favourable conditions for organotrophic denitrification (organic electron donors, e.g. dissolved organic carbon) due to low oxygen concentrations and high microbial availability of organic carbon (Cey et al., 1999; Mengis et al., 1999; Vidon and Hill, 2004). Trudell et al. (1986) investigated a shallow groundwater system in Ontario and showed the spatially heterogeneous character of organotrophic denitrification in the vertical dimension. Hill et al. (2000)

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placed a special emphasis on the patchiness of the denitrification process within the riparian groundwater of a Canadian stream and recommended intensified consideration of the spatial patterns of electron donors and groundwater flow paths. Both studies found some evidence that denitrification in aquifers is limited to the location of the organic carbon source.

In addition, Pauwels et al. (2000), Böttcher et al. (1990), Beller et al. (2004) and Knöller et al. (2005) found clear indication for lithotrophic denitrification (inorganic electron donors). The investigated groundwater systems were depleted in organic carbon, thus denitrification was interpreted to be fuelled by minerals containing reduced sulfur species or iron(II) as electron donor. Besides FeS, pyrite (FeS_2) has been suggested as electron donor for denitrification by a number of studies providing convincing evidence (e.g. Böttcher et al., 1990; Postma et al., 1991; Pauwels et al., 2000; Beller et al., 2004; Korom et al., 2005). However, little is known about the electron transfer mechanism between NO_3^- and FeS_2. Therefore, the feasibility of denitrification driven by pyrite oxidation has been questioned several times (Schippers and Jorgensen, 2002; Haaijer et al., 2007).

The objective of this study was to clarify whether pyrite oxidation controls denitrification processes in a carbonate buffered porous aquifer depleted in organic carbon and how hydrodynamic properties and microbial processes regulate nitrate concentrations in groundwater. Furthermore, new insights should be gained into the reaction pathways of FeS_2 oxidation in groundwater. To this end, our approach was to combine stable isotope analyses of groundwater NO_3^- and SO_4^{2-}, hydrochemical data, and tritium dated age profiles, sampled in a high-resolution multi-level well. Additionally, a drill core to a depth of 30 m was used for sampling sedimentary sulfur species for isotopic analyses.

2. Methods

2.1. Study site

The Test Field Scheyern (TFS) is located in southern Germany, close to the city of Munich. The TFS has an area of 1.53 km^2 and is composed of Tertiary sediments of the Upper Freshwater Molasse (Obere Süßwassermolasse) with fine and coarse grained horizontal layers of clay to gravel. Owing to the hilly orography, the thickness of the unsaturated zone ranges from few meters up to 60 m. The hydraulic conductivity has been determined by pumping tests, and a value of approximately 10^{-5} to $5*10^{-4}$ m/s was calculated. The regional groundwater flow direction was determined from hydraulic head measurements and shows a north-easterly direction (Jezek, 1992) (Fig. 1).

Annual precipitation is about 800 mm, and a total discharge of 300 mm/yr was determined (Hellmeier, 2001), whereas a groundwater recharge for the TSF of 75 mm/yr was estimated (Jezek, 1992).

The TFS is exclusively used for agriculture. An adjacent forested site is presumed to be the recharge area for most of the sampled groundwater flow lines.

A multi-level well (ML II) was repeatedly sampled (Fig. 1), providing 27 ports in intervals of 1 m between 4 m and 30 m below land surface (b.l.s.). Each port is covered with a nylon screen and is connected to the land surface by a teflon tube with an inner diameter of 3 mm. During drilling in Oct. 1991, the tubes were installed without removal of drilling cores, thus avoiding the disturbance of the aquifer matrix. More information concerning hydrogeological conditions of the TFS can be found in Schwientek et al. (submitted for publication).

2.2. Sampling

To investigate the processes governing nitrate concentrations in groundwater, ML II was repeatedly sampled between 2004 and 2007, using a vacuum pump. The water table was around 4 m below the land surface. For each depth (4–30 m), electric conductivity, pH, and oxygen concentrations of groundwater were measured in the field. Subsequently, up to 5 l of groundwater was collected in glass bottles for chemical and isotope analyses. Additionally, 0.5 l of groundwater was sampled for ^3H analyses.

2.3. Analytical methods

The ^3H concentrations were measured by a beta scintillation counter after electrolytic enrichment of the samples (Eichinger et al., 1982). For hydrochemical analyses, the samples were 0.45 µm filtered and measured with DIONEX DX 100 ion chromatographs for major anions (Cl^-, SO_4^{2-}, NO_3^-, NO_2^-) and cations (Na^+, K^+, Mg^{2+}, Ca^{2+}). A SHIMADZU TOC 500 was used to determine the DOC concentrations. The analytical uncertainty was ±2%.

For isotopic analyses of groundwater NO_3^- and SO_4^{2-}, sample volumes of 1 l were 0.45 µm filtered and acidified to pH ≤3 in order to remove any carbonate present. SO_4^{2-} was precipitated as $BaSO_4^{2-}$ using $BaCl_2$ (10%), filtered, and dried. NO_3^- was prepared as $AgNO_3$ according to the method described by Silva et al. (2000).

Oxygen isotope analyses of SO_4^{2-} and NO_3^- were conducted by pyrolysis IRMS (Thermo Electron MAT 253). $BaSO_4$ or $AgNO_3$ was weighed into silver capsules and quantitatively converted to CO with glassy carbon at 1450 °C. The contents of ^{34}S in SO_4^{2-} and of ^{15}N in NO_3^- were determined by combustion at 1000 °C in an elemental analyzer

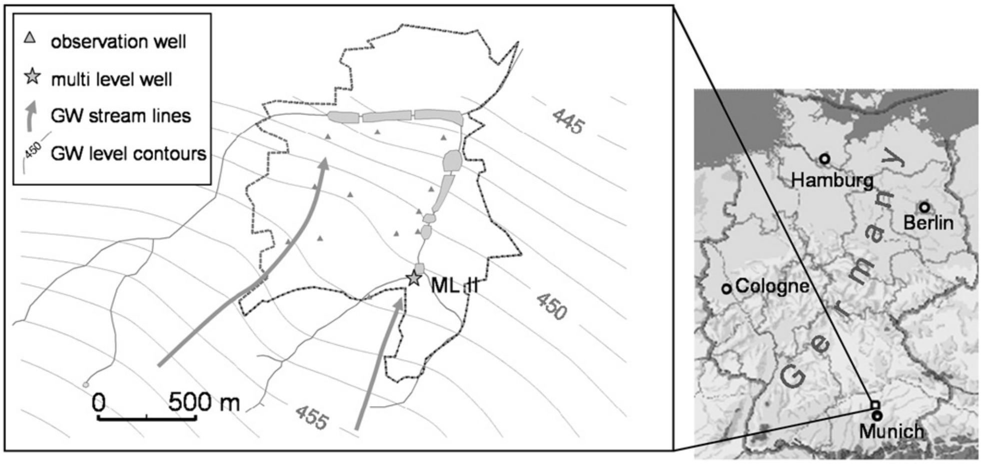

Fig. 1. Map of the Test Field Scheyern located in southern Germany with the position of the sampled multi-level well (ML II) and the groundwater flow direction. Groundwater contours are given in m asl.