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Nitrate attenuation in low-permeability sediments based on isotopic and microbial analyses

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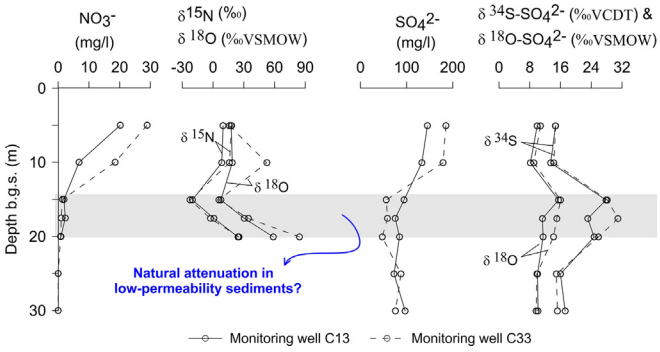
HIGHLIGHTS

- The LPS was demonstrated to have a high nitrate reduction potential.
- Denitrification was identified to be the main pathway of nitrate attenuation.
- Chemlithotrophic denitrification plays a significant role in nitrate attenuation in the LPS.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated nitrate attenuation in low-permeability sediments (LPS) in a multi-layer aquifer by integrating hydrochemical, isotopic and microbiological molecular techniques in a field site. In the meantime, the overlying high-permeability sediment (HPS) was also examined on the nitrate attenuation for the sake of comparison. Additionally, laboratory flow-through experiments were conducted to assess the overall nitrate reduction rate in the two types of sediment. The $\delta^{15}N\text{-}NO_3^-$ and $\delta^{34}S\text{-}SO_4^{2-}$ values were more enriched by approximately 37‰ and 15‰ in the LPS than the overlying HPS associated with substantial reductions of the NO_3^- and SO_4^{2-} concentration, indicating the occurrence of strong bio-reductions in nitrate and sulfate. The microbial community diversity analyses showed a higher diversity of the denitrifiers encoding *nirS*- (Shannon Index $SI = 6.3$) and *nrf*-type gene ($SI = 2.7$), and the sulfate reduction bacteria (SRB) encoding the *dsr* gene ($SI = 6.4$) in the LPS than in the HPS. The bacterial community structure was influenced by the groundwater hydrochemistry and the redox conditions. Due to the presence of anoxic groundwater with low levels of nutrients, the LPS featured higher abundances of nitrate reducers belonging to *Alphaproteobacteria* and SRB belonging to the strictly anaerobic class *Clostridia* relative to the HPS. Notably, chemolithotrophs were abundant in the LPS and likely coupled the reduction of nitrate with the oxidation of iron. Furthermore, the LPS was demonstrated to attenuate nitrate at a rate two times of the HPS in flow-through experiments, and denitrification accounted for approximately 93% of the nitrate reduction. The high nitrate reduction rate of the LPS was likely attributable to its high functional genes diversity.

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This study confirmed the occurrence of strong nitrate attenuation in the LPS. The LPS was found to play a significant role in protecting aquifers from anthropogenic contamination.

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1. Introduction

The elevated concentration levels of nitrate in groundwater pose significant threats to aquifers from which drinking water is extracted (Rivett et al., 2008). The fate of NO_3^- in low-permeability sediment (LPS), typically consisting of silty and clayey deposits, is of particular interest because aquifers are assumed to be protected from anthropogenic contamination by overlying LPS (Robertson et al., 1996; White et al., 2008). The attenuation of NO_3^- in groundwater has been widely observed in many aquifers (Green et al., 2008; Kim et al., 2009; Nolan and Hitt, 2006; Schaider et al., 2014; Zhang et al., 2009) and in LPS (Dragon, 2013; Feast et al., 1998; Rodvang and Simpkins, 2001), particularly at the boundary between the aquifer and LPS (Hendry et al., 1984; Hill et al., 2000; McMahon, 2001).

In fact, the LPS (e.g., clayey sediments) adjacent to (underlying/overlying) high-permeability zone (HPS, e.g., sand deposit) has also been revealed to be a hot spot of degradation of other contaminants as well, e.g., chlorinated hydrocarbons (Scheutz et al., 2010; Wanner et al., 2016). The attenuation potential of the LPS is thought to be restricted by the small pore sizes of clayey sediments and limited nutrient availability, which may inhibit microbial growth (Lima and Sleep, 2007). However, the LPS in aquifers is believed to greatly influence the attenuation of contaminants because of the effective occurrence of bioreactions and redox zonation resulting from dissolution of minerals in sediments (Hunkeler et al., 2004; Yan et al., 2016). Hence, the degradation capability of LPS remains debated within the scientific community and merits further study.

Nitrate in groundwater could be reduced through processes of denitrification, dissimilatory nitrate reduction to ammonium (DNRA) and anaerobic ammonium oxidation (ANAMMOX). Denitrification is usually considered the primary nitrate removal mechanism in groundwater (Seitzinger et al., 2006), which could be driven by both organic carbon and inorganic electron donors, such as reduced iron and sulfur (Korom, 1992). And a number of studies demonstrated the contribution of DNRA (An and Gardner, 2002; Burgin and Hamilton, 2007) and ANAMMOX (Smith et al., 2015; Zhu et al., 2015) to nitrate removal. The occurrence of all these transforming pathways requires the attendance of microbial communities. Functional genes analysis has been increasingly applied in the study of contaminant attenuation in groundwater (Einsiedl et al., 2015; Herrmann et al., 2015, 2017; Kim et al., 2015). Microbial activity has been recognized to play a significant role in shaping groundwater geochemistry (Akob and Kuesel, 2011; Flynn et al., 2014), which in turn, influences the microbial biodiversity patterns in groundwater. The characterization of groundwater microbial community diversity based on functional genes provides new insights into the relationship between the groundwater environment and the microbial metabolism (Herrmann et al., 2017). Changes in the community structure and the relative abundance of certain species are indicators of the nutrient levels, contaminant concentrations and bio-reduction potential. Hence, the functional genes analysis was used for evaluating the bio-reduction potential and identifying the nitrate removal pathways in the groundwater environment. The *nirS* gene was selected as the functional biomarker for denitrification since it has been demonstrated to be responsible for a key enzyme in the reduction of NO_2^- to NO during denitrification (Braker et al., 1998; Hauck et al., 2001; Herrmann et al., 2017). The presence of microbial communities that have dissimilatory nitrate reduction to ammonium (DNRA) potential was evaluated based on the *nrf* gene (Mohan et al., 2004).

In order to identify the sources of nitrate and occurrence of biodegradation of nitrate and other possible electron acceptor like sulfate in groundwater, stable isotopic analyses were applied in conjunction with the functional genes analysis. The use of multiple isotopes, i.e., ^{15}N and ^{18}O in NO_3^- and ^{34}S and ^{18}O in SO_4^{2-}, although not always conclusive, have been used to successfully discriminate among different sources (Kim et al., 2015; Ma et al., 2016; Stoewer et al., 2015) and to identify relevant bio-reduction processes (Caschetto et al., 2017; Guo et al., 2016; Palau et al., 2010). The stable isotopic fractionation of S and O has also been successfully used to elucidate the biogeochemical pathways of sulfur cycling in various ecosystems (Knoeller et al., 2008; Zhang et al., 2015). For instance, the $\delta^{34}S$ and $\delta^{18}O$ values of the remaining dissolved sulfate have been used to assess the occurrence of dissimilatory sulfate reduction (Choi et al., 2011; Einsiedl et al., 2015). And the *dsr* gene was used to assess the sulfate reduction bacteria (SRB) communities as it has been demonstrated to be a suitable biomarker for SRB (Einsiedl et al., 2015).

The objective of this study was first to examine the occurrence of natural attenuation of nitrate in the LPS and HPS via field investigations in a multi-layer aquifer. Secondly, the bio-reduction potential of the LPS and HPS in attenuating nitrate were evaluated and compared to provide a reference for the agricultural control and groundwater management. To achieve the two goals, the hydrochemical analysis and coupled multi-isotopic method were used to characterize the redox zonation and to identify potential attenuation processes in the LPS and HPS. The microbial composition based on functional genes (*nirS* and *nrf*) targeting nitrate-reducing bacteria was analysed in groundwater from the HPS and LPS to determine the bio-reduction potentials with respect to nitrate. In addition, the *dsr* gene targeting the SRB was analysed to see whether sulfate reduction occurred as well in such groundwater conditions. Finally, laboratory flow-through experiments were conducted with the HPS and LPS to access the overall nitrate reduction rate of the two types of sediment.

2. Material and methods

2.1. Site description and sampling

Groundwater and sediment samples were extracted from the multi-aquifer system at the Tongzhou (TZ) test site near Beijing (Fig. 1a). This site is part of the Integrated Field Research Platform of the Chinese Ministry of Land Resources (MLR). HPS and LPS samples were collected from sediment cores during a hydrogeological field survey. The sediments were sealed and stored in a − 80 °C freezer and thawed at 4 °C before use in the experiments. The HPS and LPS consist of yellowish-brown fine sand and dark-grey silty clay, respectively.

Two multilevel continuous multichannel tubing (CMT) systems (GHTE, Solinst, Canada), referred to as C13 and C33, from the installed CMT matrix were selected for this study (Fig. 1a). Illustrations of the CMT structure and aquifer stratigraphy are shown in Fig. 1b and c, respectively. Sampling campaigns were performed in December 2015 and June 2016 to examine nitrate variations in the two seasons. Groundwater at different levels in the multi-aquifer system was extracted from individual sampling ports (L1, L2, …, L7) of the CMT wells using an inertial pump (Lu et al., 2016). The water was directed into a flow-cell for the measurement of water temperature, pH, electronic conductivity (EC) and dissolved O_2 (DO) in the field using a Multi 350i instrument (WTW, Germany). The redox potential (Eh) was measured with a smart portable probe (BRPSCAN-10, BELL Analytical Instruments Co. Ltd., Dalian, China).

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