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A multi-isotopic approach to investigate the influence of land use on nitrate removal in a highly saline lake-aquifer system

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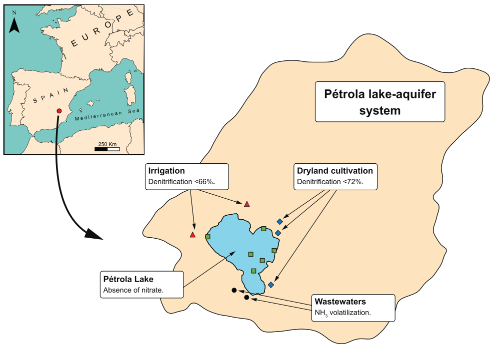
HIGHLIGHTS

- Density-driven down flow transports chemicals involved in nitrogen cycling.
- Nitrate removal processes are associated to the freshwater-saltwater interface.
- The geometry of the freshwater-saltwater interface is influenced by land use.
- Natural attenuation of nitrate is mainly linked to agricultural areas.

GRAPHICAL ABSTRACT



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ABSTRACT

Endorheic or closed drainage basins in arid and semi-arid regions are vulnerable to pollution. Nonetheless, in the freshwater-saltwater interface of endorheic saline lakes, oxidation-reduction (redox) reactions can attenuate pollutants such as nitrate (NO_3^-). This study traces the ways of nitrogen (N) removal in the Pétrola lake-aquifer system (central Spain), an endorheic basin contaminated with NO_3^- (up to 99.2 mg/L in groundwater). This basin was declared vulnerable to NO_3^- pollution in 1998 due to the high anthropogenic pressures (mainly agriculture and wastewaters). Hydrochemical, multi-isotopic ($\delta^{18}O_{NO3}$, $\delta^{15}N_{NO3}$, $\delta^{13}C_{DIC}$, $\delta^{18}O_{H2O}$, and $\delta^{2}H_{H2O}$) and geophysical techniques (electrical resistivity tomography) were applied to identify the main redox processes at the freshwater-saltwater interface. The results showed that the geometry of this interface is influenced by land use, causing spatial variability of nitrogen biogeochemical processes over the basin. In the underlying aquifer, NO_3^- showed an average concentration of 38.5 mg/L ($n = 73$) and was mainly derived from agricultural inputs. Natural attenuation of NO_3^- was observed in dryland farming areas (up to 72%) and in irrigation areas (up to 66%). In the Pétrola Lake, mineralization and organic matter degradation in lake sediment play an important role in NO_3^- reduction. Our findings are a major step forward in understanding freshwater-saltwater interfaces

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as reactive zones for NO_3^- attenuation. We further emphasize the importance of including a land use perspective when studying water quality-environmental relationships in hydrogeological systems dominated by density-driven circulation.

1. Introduction

Saline lakes have an important geochemical influence on water resources, ecological dynamics, and economic activities around the world (Jones and Deocampo, 2003). The volume of inland saline waters worldwide (about 104,000 km^3) is similar to the volume of freshwaters (Williams, 1996). Saline wetlands are mostly located in arid and semi-arid regions associated to endorheic basins, since these basins are closed drainage areas with no outlet other than evaporation (Eugster and Hardie, 1978; Yechieli and Wood, 2002). At the same time, these are environments highly vulnerable to pollution due to their low precipitation and high evaporation rates (Schütt, 1998).

The understanding of freshwater-saltwater interfaces in saline wetlands is important to comprehend shallow hydrogeological processes (Cartwright et al., 2009). Physical and biogeochemical processes control the chemical evolution of lakes and the groundwater of the connected aquifer (Castanier et al., 1993; Güler and Thyne, 2004; Skidmore et al., 2010). Solutes can enter into lakes through precipitation, surface runoff (e.g. irrigation returns and wastewater spills) and groundwater. In saline lakes, solutes also can be transported by density-driven flow (DDF) from the surface lake water to deep zones of the aquifer through the freshwater-saltwater interface (Wood and Sanford, 1990; Avrahamov et al., 2014; Colombani et al., 2015).

Andersen et al. (2005) and Santoro (2010), among others, have shown that the freshwater-saltwater interface in estuarine and coastal environments is a favorable area for oxidation-reduction (redox) reactions using organic carbon as electron donor, but little is known on the biogeochemical functions of this interface in saline inland lake systems. In aquatic environments, the redox reactions follow a sequence based on thermodynamic principles that may also follow temperature gradients (Stumm and Morgan, 1981; Orozco-Durán et al., 2015; Daesslé et al., 2017). There are, however, also contradictory findings on this redox sequence as the reduction of different electron acceptors may occur simultaneously (Postma and Jakobsen, 1996).

NO_3^- is one of the main pollutants affecting surface and groundwater due to its negative effects on human health (Fraser, 1981; Gulis et al., 2002) and on the environment. It causes eutrophication of inland waters (Ryther and Dunstan, 1971; Smith, 1998). Under anaerobic conditions, NO_3^- can be reduced through microbial processes. The main natural attenuation process in aquatic environments is denitrification, which is mainly limited by the electron donors' availability (Korom, 1992; Rivett et al., 2008). Denitrifiers can obtain metabolic energy from: i) oxidation of organic compounds (chemoorganotrophic heterotrophs), or ii) oxidation of inorganic compounds (chemolithotrophic autotrophs). Heterotrophic denitrification is linked to organic matter oxidation (Eq. (1)), whereas autotrophic denitrification is related to the oxidation of reduced such as inorganic sulfur compounds (Eq. (2)).

$$5CH_3COO^- + 8NO_3{}^- + 8H^+ \rightarrow 4N_2 + 5HCO_3{}^- + 5CO_2 + 9H_2O \quad (1)$$

$$5FeS_2 + 14NO_3{}^- + 4H^+ \rightarrow 7N_2 + 10SO_4{}^{2-} + 5Fe^{2+} + 2H_2O \quad (2)$$

In aquatic environments, NO_3^- can be also affected by other processes such as dissimilatory nitrate reduction to ammonium (DNRA) (Burgin and Hamilton, 2007). DNRA involves the transformation of NO_3^- to ammonium (NH_4^+) both by heterotrophic organisms, which use organic carbon as the electron donor (fermentative DNRA) (Eq. (3)), and by chemolithoautotrophic organisms, which use nitrate to oxidize sulfide or other reduced inorganic substrates (Eq. (4)).

$$CH_3COO^- + NO_3{}^- + 2H^+ \rightarrow NH_4{}^+ + HCO_3{}^- + CO_2 \quad (3)$$

$$3FeS_2 + 8NO_3{}^- + 32H^+ \rightarrow 8NH_4{}^+ + 6SO_4{}^{2-} + 3Fe^{2+} \quad (4)$$

Contrary to denitrifying bacteria, fermentative bacteria responsible for DNRA are strict anaerobes (Hill, 1996). Heterotrophic DNRA seems to be promoted when NO_3^- is limited and organic carbon is in excess, whereas denitrification is the dominant process when organic carbon is the constraining factor (Tiedje, 1988; Korom, 1992; Kelso et al., 1997). The prevalence of one or the other can be predicted by the organic C:N ratio of available substrates (Tiedje, 1982; Kraft et al., 2011; van den Berg et al., 2016). Prior studies suggested that DNRA may be as important, if not more dominant, than denitrification as a sink for NO_3^- in reducing environments with high sulfide contents (Brunet and Garcia-Gil, 1996; Trimmer et al., 1998). The available research recognizes the role of other microbial processes that remove NO_3^- in aquatic ecosystems, such as anaerobic ammonium oxidation (Anammox; Jetten et al., 1998) and NO_3^- reduction coupled to iron and manganese oxidation (Postma et al., 1991; Weber et al., 2006).

The analysis of stable isotopes coupled to hydrochemical investigations is a widely accepted approach to understand biogeochemical processes in groundwater. Multi-isotopic analyses have been applied to elucidate NO_3^- sources (Vitòria et al., 2004; Kendall et al., 2007) as well as to trace major biogeochemical cycles and their related bacterial-mediated redox reactions in aquifers and surface water systems (Jurado et al., 2013; Puig et al., 2013; Hosono et al., 2014; Caschetto et al., 2017).

The Pétrola endorheic basin, which was declared a nature reserve in 2005 (Spanish Decree 102/2005, September 13th), is located in a zone vulnerable to NO_3^- pollution, where fertilizer use is restricted since April 2011 (Order 2011/7/2 CMA). Previous studies have shown the potential of sediments in the Pétrola basin to promote NO_3^- attenuation at the laboratory scale (Carrey et al., 2013, 2014, 2014). Gómez-Alday et al. (2014) confirmed heterotrophic denitrification at the field scale, where density-driven flow from surface lake waters towards the underlying aquifer played an important role in solute transport. Nonetheless, the main NO_3^- reduction pathway in the Pétrola Lake remains unknown (Valiente et al., 2016). Previous studies in the Pétrola basin (Valiente et al., 2017) highlighted the importance of bacterial sulfate-reduction (BSR) processes in lake sediments and groundwater below the lake. These BSR processes were carried out, among others, by *Desulfovibrio* spp., which have also been identified as being responsible for dissimilatory NO_3^- reduction to NH_4^+ (McCready et al., 1983).

The goal of this paper was to identify the unusual ways of nitrogen removal in the Pétrola saline lake-aquifer system as an example of natural biodegradation of NO_3^- at the freshwater-saltwater interface. The effects of anthropogenic pressure on geochemical processes and solute transport may be extrapolated to other systems dominated by density-driven circulation around the world. To that end, hydrochemical, multi-isotopic and geophysical techniques were applied to trace the redox processes in the Pétrola basin. Hydrochemical and multi-isotopic techniques are highly suitable to trace pollution sources while geophysical tools may help to understand the geometry of the freshwater-saltwater interface.