Kinetics of inorganic nitrogen turnover in a sandy seepage face on a subterranean estuary

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ABSTRACT

Subterranean estuary seepage faces are recognized as important reactive interfaces that regulate solute transport to coastal ecosystems via Submarine Groundwater Discharge (SGD). Here we describe benthic processes and rates driving the biogeochemical regulation of SGD-borne inorganic N loading into the Ria Formosa lagoon (Iberian peninsula) through a sandy seepage face. Maximum potential NO_3^- reduction rates, obtained by kinetic modeling of advection-controlled flow-through reactor experiments, ranged from 2.33 ± 1.06 to 14.17 ± 0.22 nmol cm^{-3} "bulk" sediment (bs) h^{-1}. Maximum potential nitrification ranged from 0 to 7.5 ± 1.3 nmol cm^{-3} bs h^{-1} while potential ammonium assimilation was valued at 2.0 ± 0.3 nmol cm^{-3} bs h^{-1}. These NO_3^- reduction rates are in good agreement with previous estimates obtained by diagenetic modeling of in-situ porewater NO_3^- vertical profiles at the same location. Potential NO_3^- reduction rates were very sensitive to temperature ($Q_{10} = 3.5 \pm 0.2$). Porewater velocity seems to control net NO_3^- reduction rates, probably by determining solute distribution but also its supply to the microbial community by shaping the diffusive boundary layer around sediment particles. Nevertheless, NO_3^- reduction rates seem ultimately limited by organic matter availability at high velocities. Half-saturation constants of NO_3^- for NO_3^- reduction were low, suggesting that the NO_3^- reducing microbial community had high affinity for NO_3^-. In addition, our experiments provide evidence for the occurrence of alternative NO_3^- reduction pathways, including Dissimilatory Nitrate Reduction to Ammonium (DNRA) and apparent aerobic NO_3^- reduction within the shallow subsurface sediment layer (2–12 cm depth).

1. Introduction

Submarine Groundwater Discharge (SGD, *sensu* Burnett et al., 2003) is now recognized as a globally important transport vector of freshwater and solutes to the coastal zone (e.g., Moore, 2010; Kwon et al., 2014). Due to the inefficient use of fertilizers and ensuing widespread NO_3^- pollution of coastal aquifers observed worldwide, SGD has been putatively linked to the decline in water quality and trophic status of several coastal ecosystems (Hwang et al., 2005; Moore, 2010; Rocha et al., 2015). SGD is increasingly recognized as a relevant transport vector of nutrients to coastal systems and considered in current biogeochemical budget studies (e.g. Swaney and Giordani, 2011). Nevertheless, the direct quantification of Dissolved Inorganic Nitrogen (DIN) transport to the coastal zone by application of simplified mass balances, in which the non-conservative nature of DIN is ignored, to coastal aquifer systems may result in flawed predictions of N transport to surface waters. This is due to the active biogeochemical processing of DIN that occurs in the subterranean estuary (Bowen et al., 2007; Kroeger and Charette, 2008; Rocha et al., 2009), the subsurface mixing zone between groundwater and seawater (Moore, 1999). Available estimates of NO_3^- reduction rates occurring in subterranean estuaries are high, and occasionally drive significant reduction of SGD-borne NO_3^- fluxes to the coastal zone (Kroeger and Charette, 2008; Erler et al., 2014). However, there is also evidence that the magnitude of attenuation of NO_3^- loading through the seepage face, assumed to be mainly the result of heterotrophic denitrification, may be limited since other NO_3^- reducing pathways might coexist (Rocha et al., 2009; Sáenz et al., 2012; Ibánhez et al., 2013).

Although the autotrophic Anaerobic Ammonium Oxidation (anammox) process has been specifically shown to occur in subterranean estuaries (Kroeger and Charette, 2008; Sáenz et al., 2012), the occurrence of Dissimilatory Nitrate Reduction to Ammonium (DNRA) has only been inferred by mass balance and stoichiometric approaches (Bowen et al., 2007; Rocha et al., 2009; Ibánhez et al., 2013). These two processes, together with heterotrophic denitrification, are considered the main NO_3^- reducing pathways in the biosphere (although

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Nomenclature

$R_{max}^{NO_3^-}$	Maximum NO_3^- reduction rate	$R_{ox}^{NH_4^+}$	NH_4^+ oxidation rate
$K_m^{NO_3^-}$	Half-saturation NO_3^- reduction constant	R_{ads}	Kinetics rate of first order NH_4^+ adsorption-desorption
$R_{max}^{NO_2^-}$	Maximum NO_2^- reduction rate	NH_{4eq}^+	Total NH_4^+ adsorbed at equilibrium in the reactor
$K_m^{NO_2^-}$	Half-saturation NO_2^- reduction constant	NH_{4ads}^+	Total NH_4^+ adsorbed in the reactor
$R_{DNRA}^{NO_2^-}$	Maximum NO_2^- reduction to NH_4^+	K_{decay}	Hyperbolic decay inhibition factor
$K_{DNRA}^{NO_2^-}$	Half-saturation NO_2^- reduction to NH_4^+ constant	$f_{inhibition}$	Inhibition factor
		I_{nh}	Hyperbolic decay inhibition property
		R_{assim}	NH_4^+ assimilation rate

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anammox requires the prior reduction of NO_3^- to NO_2^-) (Thamdrup, 2012; Kraft et al., 2014). While anammox and heterotrophic denitrification act as sinks of bioavailable DIN, DNRA reduces NO_3^- to NH_4^+, thus recycling N into bioavailable forms and extending its residence time in the biosphere. Organic C and NO_3^- loading, together with temperature, seem to be the main factors determining the relative significance of these three processes (Kraft et al., 2014; Hardison et al., 2015). Thus, the ratio between organic C and NO_3^- availability might yet drive sequential shifting between these processes, with anammox favored at the lowest organic C to NO_3^- ratios, denitrification at intermediate ratios and DNRA at the highest (Algar and Vallino, 2014).

Due to the commonly low organic carbon concentrations found in permeable sediments, DNRA would at first glance be expected to play a minor role in processing NO_3^- loads in transit through subterranean estuaries (Santoro, 2009). However, the role of porewater advection in regulating substrate availability and driving reaction rates is not well resolved in these systems, and could indeed be determinant in our understanding of the biogeochemical role of seepage faces in modulating solute transport across the land-ocean boundary (Rocha, 2008). For example, on an annual basis, we have observed periods when SGD-borne NO_3^- fluxes at a seepage face increased at this site, in spite of significant in-situ NO_3^- reduction rates (Ibánhez et al., 2013), while the occurrence of DNRA could be inferred from mass balance and stoichiometric approaches (Rocha et al., 2009). The combination of DNRA with benthic organic matter remineralization would thus explain the apparent benthic enhancement of SGD-derived NO_3^- fluxes in the presence of significant NO_3^- reduction rates at the seepage face. This indicates that the ultimate role of the seepage face in subterranean estuaries in modulating benthic NO_3^- fluxes to surface waters is complex and locally variable in time and space.

Here, benthic reactivity affecting the DIN concentrations brought by inflowing groundwater was studied at a Ria Formosa (Southwestern Iberia) SGD seepage face. Flow-through reactor (FTR) experiments were complemented by mass balance and kinetic modeling of the resultant temporal dynamics of DIN compounds and used in combination to a) evaluate benthic biogeochemical processes involved in the modulation of NO_3^--rich SGD fluxes and b) to constrain the influence of environmental parameters on benthic reactivity.

2. Materials and methods

2.1. Study site and sampling strategy

The sampling site is located in the lower intertidal zone of the landward side of the Ancão peninsula (37°00′04″ N, 7°88′57″ W; Fig. 1), one of two sandy spits bounding the Ria Formosa coastal lagoon and within an area affected by nitrate-rich SGD (Leote et al., 2008; Rocha et al., 2009). NO_3^- and NH_4^+ content of up to 187 μM and 40 μM respectively were measured in the water seeping at the sampling site, with salinities as low as 16.8 (Leote et al., 2008). Sediment at the sampling site is composed mainly by medium-coarse sand (0.5 mm average grain size) with high hydraulic conductivity (1×10^{-3} cm s^{-1} in the top 20 cm; Rocha et al., 2009). Low standing stocks of particulate organic matter and low intermonth variability (< 0.8%; Ibánhez and Rocha, 2014a) characterized the sampled sediment during this study

(October 2010 and January 2011).

A definition of the apparent vertical biogeochemical zonation present between 0 and 20 cm depth at the studied seepage face was achieved by diagenetic modeling of in situ NO_3^- porewater profiles from 0 to 20 cm depth (Ibánhez et al., 2013). Net NO_3^- production appeared restricted to the top 1–2 cm of the sediment column, while NO_3^- reduction was the dominant process in the underlying sediment layers down to 20 cm depth. Some of the in-situ porewater NO_3^- profiles also showed an apparent limitation of NO_3^- reduction with depth, particularly during the warmer months (Ibánhez et al., 2011, 2013). In these cases, the inclusion of a non-reactive sediment layer in depth in the diagenetic models significantly improved model fit of the data, and suggested that active NO_3^- reduction would be restricted to the top 12–15 cm deep sediment layer. On this basis and for this study, the sediment depth of interest was defined as the layer between 2 and 12 cm below the surface. Porosity measured in dedicated sediment cores taken from the site in October 2010 and January 2011 (Ibánhez and Rocha, 2014a) showed vertical uniformity at this depth (2–12 cm), with values approximating 0.3.

2.2. Sediment FTR experiments

A series of FTR experiments (experiments 2 and 9) were conducted in October 2010 and January 2011 (experiments 1 to 8). A complete
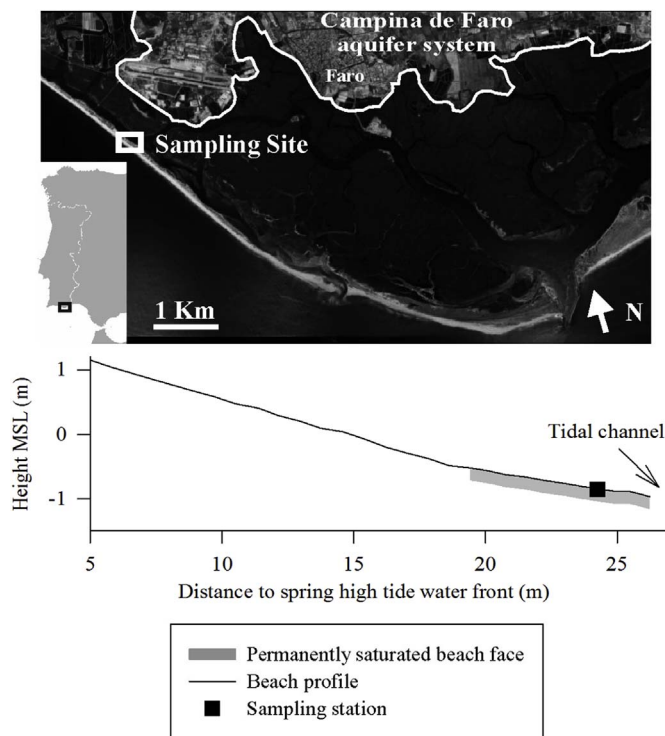

Fig. 1. Sampling site location at the inner part of Ancão peninsula, Ria Formosa coastal lagoon (SW Iberian peninsula). The location of the sampling station within the beach profile is also shown.