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Seasonal enhancement of submarine groundwater discharge (SGD)-derived nitrate loading into the Ria Formosa coastal lagoon assessed by 1-D modeling of benthic NO_3^- profiles

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ABSTRACT

The role of benthic sandy ecosystems in mitigating NO_3^- loads carried by Submarine Groundwater Discharge (SGD) to coastal marine ecosystems is uncertain. Benthic biogeochemical mediation of NO_3^--rich submarine groundwater discharge was studied at the seepage face of a barrier island site in the Ria Formosa coastal lagoon (Southern Portugal). Preliminary analysis of NO_3^- porewater distributions at the seepage face during discharge indicated that benthic biogeochemical processes could significantly affect the fluxes of groundwater-borne NO_3^- into the lagoon. In order to discriminate between the relative contribution of transport and reaction processes to shape and concentration range evidenced by in-situ porewater NO_3^- gradients, an advection-dispersion-reaction (ADR) model of NO_3^- diagenesis was applied to describe NO_3^- porewater profiles obtained in March, June, September and December 2006. Good agreement between modeled and measured profiles was obtained. Model-derived apparent benthic nitrification and NO_3^- reduction rates ranged from 0.01 to 5.2 mmol m^{-2} h^{-1}, sufficient to explain gross observed changes in NO_3^- fluxes arriving at the seepage face (up to 70% within the surficial 20 cm depth layer). Results of the analysis indicated that the upper limit of the seepage face promoted mitigation of NO_3^- fluxes to the lagoon throughout the year. In contrast, the lower limit of the seepage area promoted net amplification of the NO_3^- fluxes into the lagoon in June and September. These results will help constrain further work aiming to clarify the role of permeable sediments in mitigating nitrogen loading of coastal ecosystems.

1. Introduction

The discharge of groundwater to the coastal sea has been recently identified as an important source of fresh water and associated solutes to the coastal zone (i.e. Cable et al., 1997; Gallardo and Marui, 2006; Taniguchi et al., 2006; Niencheski et al., 2007). The difficult identification along with the spatial and temporal variability of the groundwater discharge explain the previous gap in knowledge about this fresh water source to the coastal zone (Burnett et al., 2003). Groundwater discharge to the coast occurs wherever a coastal aquifer is connected to the sea with a positive head related with the sea level (Johannes, 1980). At the exit point, sea water can infiltrate the aquifer, and the resulting mixed water seeping out at discharge sites usually contains a large proportion of recirculated sea water. This phenomenon is termed Submarine Groundwater Discharge (SGD; Burnett et al., 2003). Global estimations suggest that SGD could represent 5–10% of the total fresh water discharge to the coast (Taniguchi et al., 2002; Slomp and Van Cappellen, 2004). Since groundwater nutrient concentrations are generally higher than those found in surface waters, the groundwater contribution may rival riverine inputs in terms of nutrient transport to the coastal zone at a local level (Slomp and Van Cappellen, 2004; Moore, 2006; Swarzenski et al., 2006). Because of its potential impact on the trophic status of receiving coastal waters, quantification of the contribution of groundwater-derived nutrients to the coastal budget is an important issue (Verhoeven et al., 2006; Bowen et al., 2007).

High NO_3^- concentrations in coastal aquifers are reported worldwide (Rivett et al., 2008). Intensification of agriculture since mid-20th century has lead to diffusive NO_3^- pollution of aquifers (Foster, 2000). Other sources such as sewage and mains leakage, septic tanks, industrial spillages or the use of manure and sewage

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sludge inland can also contribute to the commonly observed high NO_3^- concentration in aquifers (Wakida and Lerner, 2005). Since denitrification is assumed to be the main pathway in mitigating NO_3^- pollution within the aquifers (Rivett et al., 2008), limited NO_3^- removal is likely to occur prior to arrival at the coastal zone mainly due to a lack of labile dissolved organic matter (Slater and Capone, 1987; DeSimone and Howes, 1996). At SGD seepage faces, tidal and wave pumping and dispersion can promote a complex mixing pattern of sea water and groundwater in the sediment (Cartwright et al., 2004; Robinson et al., 2007). Sea water infiltration can thus introduce oxygen and pelagic organic matter into the sediment and promote a complex physical and chemical zonation that, in turn, can control the resulting NO_3^- loads to the exterior (Moore, 1999; Yamashita and Tanoue, 2008; Santos et al., 2009). This mixing area is termed the subterranean estuary due to the analogy with surface estuaries (Moore, 1999).

Subterranean estuaries have been recognized as zones of important biogeochemical reactions between the mixed waters and aquifer solids (i.e. Charette et al., 2005; Charette and Sholkovitz, 2006). In particular, recent research has identified seepage faces as zones of strong nitrogen processing within the sediment prior to discharge (Ullman et al., 2003; Bowen et al., 2007; Kroeger and Charette, 2008; Spiteri et al., 2008; Rocha et al., 2009). Due to the complex solute transport and biogeochemical zonation established at the seepage face, SGD sites have been identified as zones of potentially overlapping N reactive processes and pathways, including denitrification, anaerobic ammonium oxidation (ANAMMOX) or dissimilatory NO_3^- reduction to ammonium (DNRA) (Bowen et al., 2007; Kroeger and Charette, 2008; Rocha et al., 2009). The possible overlapping of different reactive pathways with different end-products involving land-derived NO_3^- processing in SGD places raises uncertainness about the mediation role of the seepage face.

Here, seasonal nitrate benthic biogeochemistry is explored in a SGD seepage site by modeling nitrate distribution in the porewater. Mechanical dispersion, caused by the heterogeneous movement of the water in porous media (Roychoudhury, 2001), can promote solute gradients that can be misinterpreted as caused by benthic reactivity. Therefore, an Advection-Dispersion-Reaction (ADR) model inclusive of a free-boundary solution is used in order to elucidate the relative contribution of transport and reaction processes in nitrate porewater distribution. The main objective of this study is to obtain preliminary seasonal explanations of the benthic reactivity and interfacial fluxes in nitrate-rich SGD seepage sites, and to estimate the mediation role of the benthic community in modulating land-derived N loads to the coastal area.

2. Methods

2.1. Field sampling

Field sampling was carried out at a site located in the inner intertidal face of the Ancão peninsula (37°00′04″N, 7°88′57″W), one of the two sandy peninsulas framing the Ria Formosa coastal lagoon (Fig. 1). The nearby coastal area has a semi-diurnal, mesotidal regime, an attribute that promotes a water renewal rate varying between 52 and 80% of the total volume of the lagoon (Andrade et al., 2004) and creates an extensive intertidal zone. The area is affected by nitrate-rich SGD (Leote et al., 2008). Large amounts of nitrate associated with low salinity water seep out during low tide (Leote et al., 2008; Rocha et al., 2009). Sediment at the sampling site is characterized by medium-coarse sand ($d_p = 0.5$ mm), with high permeability (3.2×10^{-3} cm s^{-1}).

Salinity and NO_3^- porewater profiles and seepage rate measurements and associated fluxes were carried out at the sampling site during March, June, September and December 2006. General sampling work was conduced during two consecutive tidal cycles at the intertidal seepage face during sediment exposure. Two sites in the permanently saturated sediment surface affected by SGD were selected, viz: A, located at the lowest part of the beach profile, close to the observed point at which the discharge peaks and B, at the upper limit of the discharge zone.

2.1.1. Porewater solute profiles

Porewater samples were taken in-situ using soil moisture samplers (Rhizon SMS-10 cm; Rhizosphere, 0.1 μm pore size). The samplers were placed into the sediment at fixed depths via two in-situ acrylic profilers modified from the design of (Seeberg-Elverfeldt et al., 2005), situated at each sampling location (Fig. 1). Each profiler was buried in-situ with 12 Rhizon membrane samplers located horizontally at vertical intervals of 1, 2.5 and 5 cm, covering the first 20 cm depth of the sediment column. The samplers provide the advantage of remaining in place throughout the entire field experiment, thus causing minimal disturbance over the local benthic flow patterns (Cappuyns et al., 2004; Seeberg-Elverfeldt et al., 2005). Porewater was collected at each depth by connecting a sterile, 11 ml vacuum flask (BH Vaccutainer) to the Rhizon membranes through connection tubing protruding from the sediment surface. The first milliliter, corresponding to the dead volume inside the tubing and filtration device ensemble, was discarded to avoid contamination of consecutive samples (Seeberg-Elverfeldt et al., 2005). The final porewater aliquots (5–6 ml at each depth), sealed inside the vacuum tubes, were then stored at 4 °C until analysis. The pore size of the filtration membranes together with the sampling storage in vacuum tubes permitted the collection of porewater samples ready for analysis without further preservation (Luo et al., 2003; Seeberg-Elverfeldt et al., 2005). All parameters were analyzed within 2 weeks of sampling.

2.1.2. Seepage measurements

Three to five Lee-type seepage meters (Lee, 1977) were deployed at the beach face (Fig. 1) to allow direct measurement of advective velocities and solute fluxes across the sediment-water interface (Lee, 1977; Burnett et al., 2006; Taniguchi et al., 2006). These were deployed at low tide in alignment with the porewater profilers and sampling started on the subsequent low tide following the

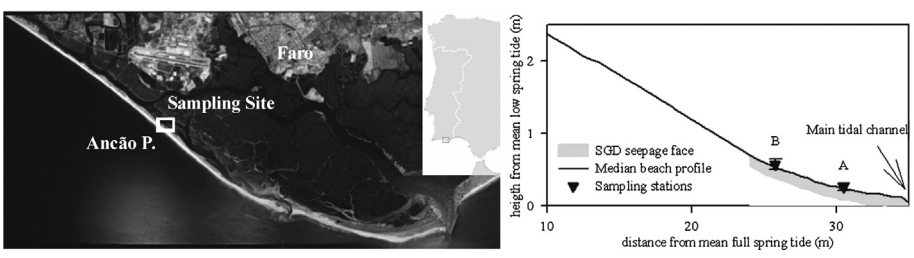

Fig. 1. Sampling site locations at the Ria Formosa coastal lagoon (South Portugal, image obtained from LandSat). Location of the two sampling stations in the median beach profile are also shown (station A, located in the main seepage face and station B, located in the upper limit of the permanently saturated seepage zone).