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Effects of recirculation of seawater enriched in inorganic nitrogen on dissolved organic carbon processing in sandy seepage face sediments

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ABSTRACT

Human activities are now the main source of bioavailable Nitrogen to Earth's ecosystems. Disruption of the N cycle can promote changes to the biogeochemical cycling of other elements in particular to the oxygen and carbon cycles. Nevertheless, information on how increasing Dissolved Inorganic Nitrogen (DIN) availability might affect the benthic processing of organic matter in coastal sandy sediments is currently unavailable. Here, we present a series of flow-through reactor experiments conducted with undisturbed sediment cores collected at an intertidal seepage face (Ria Formosa lagoon, SW Iberian Peninsula) in order to evaluate the effect of increasing DIN availability on benthic dissolved organic C (DOC) reactivity. Our results show that the metabolic activity of the benthic community can be a significant source of DOM to the porewater. Furthermore, in the absence of DIN, increasing porewater flow rates accelerated benthic DOM production and increased the recalcitrant nature of DOC transported across the sediment-water interface. In contrast, the co-occurrence of high DIN concentrations and high seepage velocities increased the microbial breakdown of organic material. Our results suggest that the availability of DIN in permeable seepage faces increases the net production of labile DOC, by enhancing the ability of the benthic microbial community to process refractory organic matter. Hence, we suggest that increasing DIN availability in coastal permeable sediments accelerates benthic organic C processing, promoting the release of more labile DOC to receiving water bodies.

1. Introduction

Coastal sediments are sites of intense processing of organic matter sourced from adjacent coastal seas or from land. Although most of the research on benthic organic matter reactivity has focused on organic-rich cohesive sediments, increasing evidence has shown coastal permeable sediments to be zones of intense organic matter processing and turnover (Boudreau et al., 2001; Rocha, 2008). In permeable sediments, porewater advection induces the rapid interchange of solutes and particles between the overlying water and the benthic compartment, thus controlling the distribution and fate of important metabolites such as O_2 and organic matter (e.g. Huettel et al., 1996; Precht and Huettel, 2003). The common low-organic matter content of coastal sands seems therefore to result from high benthic metabolic and solute exchange rates rather than result from the low reactivity of the organic C pool (Huettel and Rusch, 2000; de Beer et al., 2005).

When the availability of particulate organic matter (POM) is limited, Dissolved Organic Matter (DOM) may still play a crucial role in benthic metabolism since heterotrophic microorganisms can directly employ some of the DOM as an electron donor in redox reactions. However, little information is available on the chemical composition and reactivity of DOM in permeable sediment porewaters (e.g. Santos et al., 2009; Chipman et al., 2010; Kim et al., 2012) even though a substantial fraction of porewater DOM might be recalcitrant (Burdige, 2001; Burdige et al., 2004). Benthic microbial degradation of either POM or DOM may be responsible for the production of this refractory material (Ogawa et al., 2001; Chipman et al., 2010), thus enhancing the sequestration of fixed carbon in the oceans (Hansell, 2013).

Permeable sediments located at the land-ocean interface are particularly important as biogeochemical hotspots acting as reactive shunts intersecting different DOM delivery pathways. Indeed, local benthic metabolism may actively change the composition and reactivity of the DOM in transit to the sea from land via Submarine Groundwater Discharge (SGD, i.e. any flow of water out across the sea floor; Burnett et al., 2003) and/or originating from local marine sources (Chipman et al., 2012; Kim et al., 2012). Elucidating the transfer and cycling of DOM in permeable sediments is hence important to ultimately understand the functional role of these sediments in the coastal and oceanic C cycle.

Due to the active processing of marine and terrestrial organic matter, sandy intertidal sediments are also sites of active Dissolved Inorganic N (DIN) regeneration (de Beer et al., 2005; Santos et al., 2009). Other sources of DIN to the porewater can be linked to human activities in

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the coastal zone, such as wastewater disposal or the use of fertilizers. This anthropogenic N can enter the internal beach aquifer through direct disposal, recirculation of polluted seawater through the sediment or directly from land when a coastal aquifer is hydraulically connected to the sea (Slomp and Van Cappellen, 2004). Due to the high mobility of N compounds in the environment and the role N plays in microbial and primary producer metabolism, human disruption of the N cycle can promote changes in the cycling of other elements, particularly O and C (Falkowski, 1997; Mackenzie et al., 2002). Although substantial research has focused on understanding natural NO_3^- attenuation processes in coastal benthic systems (e.g. Bonin and Raymond, 1990; Cornwell et al., 1999; Burgin and Hamilton, 2007), to our knowledge, the impact of increased DIN availability on organic C transport and reactivity in coastal permeable sediments has not been investigated. Elucidation of the impact of DIN availability on organic matter processing in coastal permeable sediments could therefore offer valuable information on the resilience and plasticity of this coastal compartment to current and projected anthropogenic pressure.

The objectives of this study are therefore (1) to evaluate the role of intertidal permeable sediments in mediating DOM fluxes to the coastal sea and (2) to elucidate the effect of augmented DIN concentrations in the seawater circulating through the beach face on benthic dissolved organic C (DOC) processing. We performed a series of flow-through reactor (FTR) experiments to simulate active seepage through undisturbed sediment slices taken from an intertidal seepage face at the Ria Formosa coastal lagoon. The location has been subject to periodic DIN-rich SGD (Leote et al., 2008). The influence of porewater velocity and DIN concentrations over benthic DOM reactivity was experimentally evaluated by following the DOC levels at both the inlet and outlet of the experimental reactors and the makeup of the Chromophoric DOM (CDOM; the DOM fraction with measurable optical properties) pool.

2. Materials and methods

2.1. Study site

Ria Formosa (SW Iberian Peninsula; Fig. 1) is a 110 km^2 coastal lagoon separated from the Atlantic Ocean by a multi-inlet sand barrier system. The lagoon is embedded within a 760 km^2 semi-arid watershed that includes an intensively farmed coastal plain. The indiscriminate use of inorganic fertilizers led to heavy NO_3^- contamination of the main aquifer systems north of the lagoon (Almeida and Silva, 1987). Following the EU nitrate directive, the Campina de Faro aquifer system (NW Ria Formosa; Fig. 1) was designated a Nitrate Vulnerable Zone in 2001, and this was extended to the Campina da Luz aquifer system (NE Ria Formosa; not shown in Fig. 1) in 2005. Preliminary estimates of N loading through SGD suggest it to be a potentially important source of N to the lagoon (36.2 mol N $year^{-1}$ m^{-1}; Leote et al., 2008). NO_3^- and NH_4^+ content of up to 187 μM and 40 μM respectively were measured in the seeping water at the sampling site (Leote et al., 2008). The linear correlation of NO_3^- content with salinity in water samples taken from seepage meters extrapolates to a NO_3^- concentration of 422 μM at 0 salinity, indicating the potential maximum NO_3^- concentration at the site via groundwater input (Leote et al., 2008).

2.2. Flow-through benthic reactor experiments

Sediment FTR experiments were conducted in triplicate (with the exception of Experiment 1; see Table 1) from July 2010 to January 2011. The sediment used was taken from the permanently saturated intertidal area affected by periodic NO_3^--rich SGD, on the inner part of Ancão Peninsula (37°00′04″ N, 7°88′57″ W; Fig. 1). Sediment at the sampling site is composed mainly of medium-coarse sand (average grain size 0.5 mm; silt + clay < 1.7% weight; Rocha et al., 2009), with high hydraulic conductivity (1×10^{-3} cm s^{-1}; Leote et al., 2008). Undisturbed, saturated sediment cores (40 cm length, 6.6 cm inner diameter) were collected with polycarbonate core liners in the permanently saturated lower intertidal area, close to the peak discharge area at the seepage face. These were collected manually by pushing the core liners into the sediment at low tide, digging them out and immediately transfering the cores to the laboratory. There, sediment cores were sliced into three different depth intervals (0–2 cm, 2–12 cm and 12–32 cm depth), according to the vertical distribution of the C:N ratio in the POM and benthic permeability gradient previously assessed at the site (Rocha et al., 2009). An adapted HTH core slicer (HTH Teknik, Luleå, Sweden; Renberg and Hansson, 2008) was used to transfer

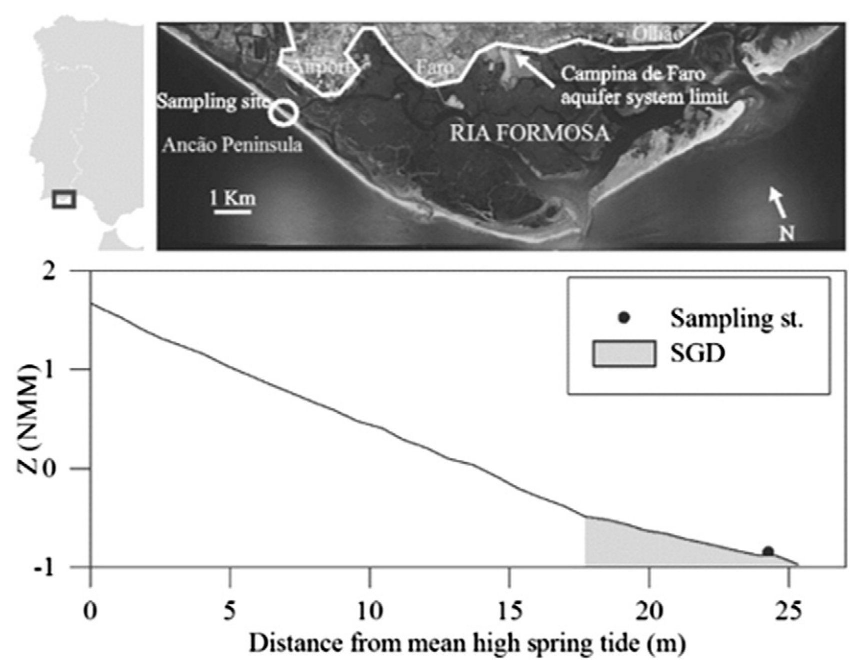

Fig. 1. Sampling location at Ancão Peninsula (Ria Formosa coastal lagoon, SW Iberian peninsula; top panel). Beach profile measured during the study along with the approximate area of the permanently-saturated seepage face is shown (bottom panel).