

## Benthic fluxes in a tidal salt marsh creek affected by fish farm activities: Río San Pedro (Bay of Cádiz, SW Spain)

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### ABSTRACT

Benthic fluxes of dissolved inorganic carbon, total alkalinity, oxygen, nutrients, nitrous oxide and methane were measured in situ at three sites of Río San Pedro salt marsh tidal creek (Bay of Cádiz, SW Spain) during three seasons. This system is affected by the discharges of organic carbon and nutrients from the surrounding aquaculture installations. Sediment oxygen uptake rates and inorganic carbon fluxes ranged respectively from 16 to 79 mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> and from 48 to 146 mmol C m<sup>-2</sup> d<sup>-1</sup>. Benthic alkalinity fluxes were corrected for the influence of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>+NO<sub>2</sub><sup>-</sup> fluxes, and the upper and lower limits for carbon oxidation rates were inferred by considering two possible scenarios: maximum and minimum contribution of CaCO<sub>3</sub> dissolution to corrected alkalinity fluxes. Average C<sub>ox</sub> rates were in all cases within ±25% of the upper and lower limits and ranged from 40 to 122 mmol C m<sup>-2</sup> d<sup>-1</sup>. Whereas carbon mineralization did not show significant differences among the sites, C<sub>ox</sub> rates varied seasonally and were correlated with temperature ( $r^2=0.72$ ). During winter and spring denitrification was estimated to account for an average loss of 46% and 75%, respectively, of the potentially recyclable N, whereas during the summer no net removal was observed. A possible shift from denitrification to dissimilatory nitrate reduction to ammonium (DNRA) during this period is argued. Dissolved CH<sub>4</sub> and N<sub>2</sub>O fluxes ranged from 5.7 to 47 μmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> and 4.3 to 49 μmol N–N<sub>2</sub>O m<sup>-2</sup> d<sup>-1</sup>, respectively, and represented in all cases a small fraction of the total inorganic C and N flux. Overall, about 60% of the total particulate organic matter that is discharged into the creek by the main fish farm facility is estimated to degrade in the sediments, resulting in a significant input of nutrients to the system.

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### 1. Introduction

Coastal sediments are in general sites of intense organic matter mineralization and nutrient recycling, and therefore play a key role in controlling coastal biogeochemistry (e.g., Berelson et al., 1998; Hopkinson et al., 1999; Codispoti et al., 2001). The measurement of solute fluxes across the sediment-water interface gives information about the role of sediment diagenesis and about the preferential pathways of organic matter mineralization. In sediments the organic matter is degraded to inorganic constituents through a vertical sequence of diverse microbial processes that use different terminal electron acceptors as oxidants (Froelich et al., 1979; Canfield, 1993). Although the most efficient of these processes is the aerobic oxidation of organic matter, in coastal sediments with high organic content the oxygen is rapidly consumed within the first millimeters of sediment (Revsbech et al., 1980) and thus microorganisms use other terminal acceptors as oxidants, such as NO<sub>3</sub><sup>-</sup>, oxides of Mn and Fe, and SO<sub>4</sub><sup>2-</sup> (Froelich et al., 1979; Canfield, 1993). Some of the NH<sub>4</sub><sup>+</sup> released from organic matter degradation is oxidized to NO<sub>3</sub><sup>-</sup> in the presence of oxygen during nitrification, which can be subsequently reduced to N-

gases (N<sub>2</sub> and N<sub>2</sub>O) during denitrification. Coastal sediments are considered in general as favorable sites for denitrification due to the high loading of nutrients and organic matter and the low oxygen concentrations (Seitzinger et al., 1984; Seitzinger, 1988). In addition to NO<sub>3</sub><sup>-</sup> reduction by denitrifiers, bacteria can also use NO<sub>3</sub><sup>-</sup> as electron acceptor in the dissimilatory nitrate reduction to ammonium (DNRA) (Jørgensen, 1989). Nitrous oxide (N<sub>2</sub>O), which is a potent greenhouse biogas (Rodhe, 1990) that it is also involved in the destruction of stratospheric ozone (Cruzten, 1970), can be produced during nitrification, denitrification and DNRA. Below the sub-oxic zone, where sediments are very reductive, sulfate reduction becomes the dominating diagenetic process and generally accounts for about 50% of organic carbon oxidation in coastal sediments (Canfield, 1993; Thamdrup and Canfield, 2000). Once sulfate is depleted organic carbon is degraded in various fermentative processes and methanogenesis to CH<sub>4</sub> and CO<sub>2</sub>. CH<sub>4</sub> can be subsequently oxidized anaerobically by sulfate-reducing bacteria (Martens and Berner, 1974), which limits its flux to the water column. In this way, besides CO<sub>2</sub> which is the main end-product of organic matter mineralization, N<sub>2</sub>O and CH<sub>4</sub> are also produced in coastal sediments in amounts that are often insignificant for the N and C-cycles of the sediments (e.g., Hopkinson et al., 1999; Alongi et al., 2005) but that may be significant for the global warming potential of coastal environments. Several authors

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have pointed out the importance of benthic mineralization processes as a major source of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  in coastal systems (Robinson et al., 1998; Seitzinger et al., 2000; Upstill-Goddard et al., 2000; Abril and Iversen, 2002; Bange, 2006). Whereas the oceans play a major role in atmospheric  $\text{N}_2\text{O}$  budget, accounting for about one third of global  $\text{N}_2\text{O}$  emissions (Seitzinger et al., 2000), oceanic  $\text{CH}_4$  emissions are only a small term (2%) in the global  $\text{CH}_4$  budget (Reeburgh, 2007). However, although continental shelves and estuaries occupy only a small portion of the world oceans, they contribute from 35 to 60% of oceanic  $\text{N}_2\text{O}$  emissions (Bange et al., 1996; Seitzinger et al., 2000) and about 75% to the global oceanic  $\text{CH}_4$  emissions (Bange et al., 1994).

In this study organic matter oxidation and nutrient fluxes across the sediment-water interface were investigated. Benthic chamber flux incubations were performed in situ during different periods of the year in a shallow tidal creek located in the salt marsh area of the Bay of Cádiz (SW Spain). This environment is affected by the inputs of organic matter and nutrients coming from aquaculture. It has been reported that inputs of residual fish food and excreta from fish farms enhance total sediment metabolism (Hall et al., 1990) and may shift the dominant microbial processes in sediments (Christensen et al., 2000). The aim of this paper is to examine the stoichiometry of diagenetic reactions in this environment, the seasonal variability in benthic fluxes and the potential impacts of aquaculture waste inputs to the system. Direct benthic fluxes of  $\text{N}_2\text{O}$  and  $\text{CH}_4$ , which are very sparse in the literature, were also measured and discussed.

## 2. Materials and methods

### 2.1. Study area

Work was carried out in Río San Pedro creek, a shallow tidal inlet located within the salt marsh area of the Bay of Cádiz (SW Spain) (Fig. 1). The creek used to be a tributary of the Guadalete river until it was artificially blocked at 12 km from the mouth, so currently the only freshwater input into the creek comes from precipitation. It is characterized by a semi-diurnal tidal regime, with the tidal height ranging from 3.5 m at spring tide to 0.5 m at neap tide. The average

depth ranges between ~3 and 5 m and the water column is well mixed. A considerable salt marsh area surrounds the creek, but it has been largely exploited by human activities so that at present Río San Pedro is considerably isolated from the marshes by human-made embankments and by a dam in the innermost part of the creek, which only allows water exchange in periods of high water level. Three fish farms are located on the banks of Río San Pedro creek. One of them, situated in the upper part of the creek (Fig. 1), is large enough to be considered as the main source of organic matter and nutrients to the system. This fish farm covers about  $1.3 \cdot 10^6 \text{ m}^2$ , and supports a culture of around  $10^6 \text{ kg yr}^{-1}$  of gilthead seabream (*Sparus aurata*). The total volume of water introduced daily by the fish farm ranges from  $180,000 \text{ m}^3$  to  $290,000 \text{ m}^3$  (Tovar et al., 2000). The fish farm consists of several batteries of shallow ponds excavated in the soil. The shallowness of the ponds, together with the high loading of organic matter due to the fish farming, is expected to cause a very intense benthic metabolism in their bottoms. The overlying water, enriched with the metabolic products coming from organic matter diagenetic processes, is directly discharged to the upper part of the creek. As a consequence, the concentration of nutrients and suspended solids in the creek is relatively high. Tovar et al. (2000) estimated the total amount of dissolved nutrients, total suspended solids (TSS), particulate organic matter (POM) and biochemical oxygen demand ( $\text{BOD}_5$ ) that the fish farm discharged into the receiving waters for each ton of cultured fish. According to this, approximately  $9.1 \cdot 10^6 \text{ kg TSS}$ ,  $8.4 \cdot 10^5 \text{ kg POM}$ ,  $2.4 \cdot 10^5 \text{ kg BOD}$ ,  $36 \cdot 10^3 \text{ kg N-NH}_4^+$ ,  $5.0 \cdot 10^3 \text{ kg N-NO}_2^-$ ,  $6.7 \cdot 10^3 \text{ kg N-NO}_3^-$  and  $2.6 \cdot 10^3 \text{ kg P-PO}_4^{3-}$  are discharged annually into the environment. In addition, De la Paz et al. (2008b) observed strong dissolved inorganic carbon concentration gradients between the creek and the Bay of Cadiz, which they related to the inputs of the fish farm effluent. These authors found that Chl-a concentrations, which ranged from 1 to  $14 \mu\text{g L}^{-1}$ , increased at neap tides, due to an enhancement of phytoplankton growth with a higher residence time of the water inside the creek. However, primary production activity seemed to be patchy and depended on the balance between nutrients and turbidity, which changed with tidal movements. Overall, they observed a strong seasonality in dissolved inorganic carbon, pH and

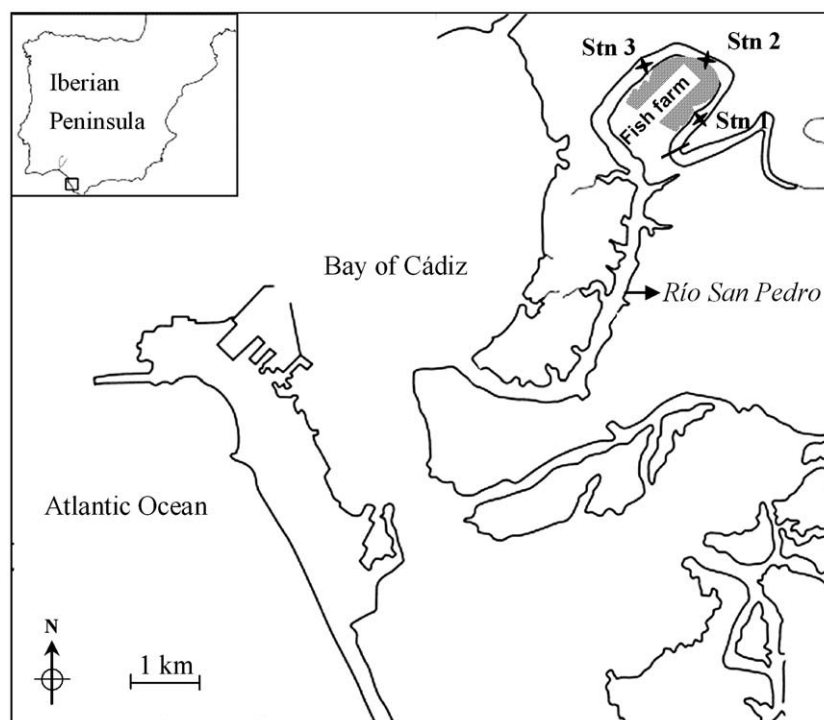


Fig. 1. Map of the Bay of Cádiz and Río San Pedro creek, showing the locations of the fish farm and the sampling stations.

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