



# Seasonal variation of early diagenesis and greenhouse gas production in coastal sediments of Cadiz Bay: Influence of anthropogenic activities



Macarena Burgos <sup>a, \*</sup>, Teodora Ortega <sup>a</sup>, Julio Bohórquez <sup>b</sup>, Alfonso Corzo <sup>b</sup>,  
Christophe Rabouille <sup>c</sup>, Jesús M. Forja <sup>a</sup>

<sup>a</sup> Dpto. Química-Física, CACYTMAR, Universidad de Cádiz, Campus Río San Pedro, s/n, Puerto Real, Cádiz, Spain

<sup>b</sup> Department of Biology, Faculty of Marine and Environmental Science, University of Cádiz, Pol. Río San Pedro s/n, 11510 Puerto Real, Spain

<sup>c</sup> Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS UNMR 1572, Av. de la Terrasse, 91198 Gif sur Yvette, France

## ARTICLE INFO

### Article history:

Received 26 January 2017

Received in revised form

26 September 2017

Accepted 18 October 2017

### Keywords:

Early diagenesis

Greenhouse gas

Microelectrodes

Coastal sediment

Anthropogenic activities

## ABSTRACT

Greenhouse gas production in coastal sediments is closely associated with the early diagenesis processes of organic matter and nutrients. Discharges from anthropogenic activities, particularly agriculture, fish farming and waste-water treatment plants supply large amounts of organic matter and inorganic nutrients that affect mineralization processes. Three coastal systems of Cadiz Bay (SW Spain) (Guadalete River, Río San Pedro Creek and Sancti Petri Channel) were chosen to determine the seasonal variation of organic matter mineralization. Two sampling stations were selected in each system; one in the outer part, close to the bay, and another more inland, close to a discharge point of effluent related to anthropogenic activities. Seasonal variation revealed that metabolic reactions were driven by the annual change of temperature in the outer station of the systems. In contrast, these reactions depended on the amount of organic matter reaching the sediments in the outermost part of the systems, which was higher during winter. Oxygen is consumed in the first 0.5 cm indicating that suboxic and anoxic processes, such as denitrification, sulfate reduction and methanogenesis are important in these sediments. Sulfate reduction seems to account for most of the mineralization of organic matter at the marine stations, while methanogenesis is the main pathway at the sole freshwater station of this study, located inside the estuary of the Guadalete River, because of the lack of sulfate as electron acceptor. Results point to denitrification being the principal process of N<sub>2</sub>O formation. Diffusive fluxes varied between 2.6 and 160 mmol m<sup>-2</sup> d<sup>-1</sup> for dissolved inorganic carbon (DIC); 0.9 and 164.3 mmol m<sup>-2</sup> d<sup>-1</sup> for TA; 0.8 and 17.4 μmol m<sup>-2</sup> d<sup>-1</sup> for N<sub>2</sub>O; and 0.1 μmol and 13.1 mmol m<sup>-2</sup> d<sup>-1</sup> for CH<sub>4</sub>, indicating that these sediments act as a source of greenhouse gases to the water column.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Coastal systems are the principal link between continents and oceans and receive inputs of particulate and dissolved organic carbon and nutrients from rivers and runoff (Cai, 2011; Dagg et al., 2004; Dai et al., 2012; McKee et al., 2004). Part of the particulate organic material settles to the seafloor in estuaries and deltas;

therefore estuarine sediments are important in terms of organic matter (OM) mineralization and nutrient recycling.

The preferential pathway of OM decomposition occurs through a vertical sequence of diverse microbial processes that use different terminal electron acceptors as oxidants (Berner, 1980; Boudreau, 1996; Froelich et al., 1979). Because the most efficient diagenetic process is the aerobic oxidation of OM, oxygen is rapidly consumed in coastal sediments with high organic matter content, and then suboxic and further anaerobic remineralization occurs (Mucci et al., 2000). Suboxic remineralization processes include denitrification, nitrate reduction and Mn and Fe oxide reduction, whereas anoxic remineralization occurs mainly by sulfate reduction and methanogenesis (Burdige, 2011) which all produce reduced compounds

\* Corresponding author.

E-mail addresses: [macarena.burgos@uca.es](mailto:macarena.burgos@uca.es) (M. Burgos), [teodora.ortega@uca.es](mailto:teodora.ortega@uca.es) (T. Ortega), [julio.bohorquez@uca.es](mailto:julio.bohorquez@uca.es) (J. Bohórquez), [alfonso.corzo@uca.es](mailto:alfonso.corzo@uca.es) (A. Corzo), [christophe.rabouille@lsce.ipsl.fr](mailto:christophe.rabouille@lsce.ipsl.fr) (C. Rabouille), [jesus.forja@uca.es](mailto:jesus.forja@uca.es) (J.M. Forja).

that are re-oxidized by oxygen. During nitrification some of the  $\text{NH}_4^+$  released from OM mineralization is oxidized to  $\text{NO}_3^-$  (Meyer et al., 2008). Both processes, nitrification and denitrification, produce  $\text{N}_2\text{O}$ , which is a potent greenhouse gas and also involved in the destruction of stratospheric ozone (IPCC, 2013).

When all potential electron acceptors, including sulfate, are depleted, the organic carbon is mineralized by methanogenesis in anaerobic conditions, producing  $\text{CH}_4$  from  $\text{CO}_2$  reduction or  $\text{CH}_4$  and  $\text{CO}_2$  from acetate fermentation (Reeburgh, 2007). Upwardly diffusing methane can be oxidized by microorganisms using sulfate or oxygen, and this limits its flux to the water column.

Besides  $\text{CO}_2$ , which is the main end-product of early diagenesis,  $\text{N}_2\text{O}$  and  $\text{CH}_4$  are also produced in coastal sediments, which may constitute a significant source of greenhouse gases to the atmosphere from coastal regions (Borges et al., 2017; Meyer et al., 2008; Regnier et al., 2013).

Several authors have pointed out the importance of benthic mineralization processes as a major source of greenhouse gases in coastal systems (Abril and Iversen, 2002; Bange, 2006; Cai et al., 2000; Upstill-Goddard et al., 2000). However, coastal environments are geomorphologically and hydrodynamically very diverse; their sedimentary conditions can be very different; and this affects the size of sediment particles, the content and preservation rate of organic matter, and the biological community that they are able to sustain. Many of these factors are known to influence greenhouse gas production and fluxes to the atmosphere (Burdige, 2011; Cai et al., 2000).

In addition, biogeochemical processes in estuarine and coastal sediments are often affected by tidal processes, river water discharges, seasonality in response to annual changes in temperature (Burdige, 2006), the composition and reactivity of carbon deposited in sediments (Kemp et al., 1997), and rates of benthic macrofaunal activity (Duport et al., 2007). Human activities, such as wastewater treatment, fish farming, harbors, industries and agriculture, all tend to increase the amounts of organic matter and nutrients that reach the coastal waters, and have an increasing influence on the marine biogeochemical dynamics (Walsh et al., 2011).

This paper reports a study of the seasonal variation of early diagenesis processes in sediments of three coastal ecosystems of Cadiz Bay influenced by different human activities (urban effluents, fish farming and agriculture). Sampling stations were located at different distances from the discharge points of urban effluents and primary sector activities, with the objective of investigating the influence of anthropogenic activities on biogeochemical cycles and the production of greenhouse gases in these sediments. Diffusive fluxes at the sediment-water interface for dissolved inorganic carbon (DIC), total alkalinity (TA),  $\text{CH}_4$ , and  $\text{N}_2\text{O}$ , have been examined.

## 2. Material and methods

### 2.1. Study site

Cadiz Bay ( $36^\circ 29' \text{ N}$ ,  $6^\circ 13' \text{ W}$ ), covering an area of  $152 \text{ km}^2$ , is characterized by semi-diurnal mesotides (average tidal range  $0.98\text{--}3.20 \text{ m}$ ). This region comprises a natural protected area (The Natural Park of Cadiz Bay,  $10522 \text{ ha}$ ) and several cities that together sustain a total population of  $425000$  inhabitants. Samplings took place in three coastal systems surrounding the bay (Fig. 1) that receive organic matter and nutrients from urban effluents and primary sector activities such as agriculture and fish farming. Water flow direction of the systems is highly dependent on the tides.

Within each system, two stations located at different distances from sources of anthropogenic inputs were sampled. In the estuary of the Guadalete River ( $18 \text{ km}$  long and maximum depth of  $6 \text{ m}$  in the river mouth), the outer station (G3) is close to El Puerto de

Santa Maria (a town of  $88700$  inhabitants in 2014), and the inner station (G6) is located near to the effluent discharge point of the wastewater treatment plant of Jerez de la Frontera (a city of  $212200$  inhabitants in 2014) which discharges its effluent into the Guadalete River. The Rio San Pedro Creek is located within the salt marsh area of Cadiz Bay and is characterized by a relatively constant depth of  $3 \text{ m}$ . The tidal current flows from the bay along the creek where the freshwater inflow is not significant, except during seasonal rains in winter. Two sampling stations were selected along the  $12 \text{ km}$  length of the system: one in the outer part (R4), and the other (R7) in the inner part of the system. The Creek receives inputs of organic matter and nutrients from the wastewater discharges of a fish farm located less than one km upstream of the station R7. The third system, the Sancti Petri Channel, is the main channel ( $18 \text{ km}$  long) running through the centre of a large zone of salt marshes ( $6000 \text{ ha}$ ) that links the inner bay with the Atlantic Ocean. The channel is deeper at both ends, reaching depths of  $7 \text{ m}$ , and very shallow in the central part (average depth of  $2 \text{ m}$ ). The outer station (S3) is located on the Atlantic side of the channel and the inner one (S6) is about  $0.5 \text{ km}$  distant from the Iro River mouth, which receives the sewage effluent of Chiclana de la Frontera (a town of  $82300$  inhabitants, year 2014).

### 2.2. Sample collection

Samples were collected during two seasonal sampling campaigns in winter and spring of 2014 (February and July). Six polycarbonate cores ( $60 \text{ cm}$  long,  $9.5 \text{ cm}$  inner diameter) were taken at each station and they were carefully maintained in vertical position during transportation to the laboratory. Two cores were used to determine  $\text{CH}_4$  and  $\text{N}_2\text{O}$  concentration profiles in duplicate. Sediment subsamples of  $5 \text{ g}$  were taken at  $1 \text{ cm}$  depth intervals. Subsamples were equilibrated in a  $20 \text{ mL}$  septum vial together with  $10 \text{ mL}$  of air, and  $5 \text{ mL}$  of seawater fixed with mercury chloride that was saturated with a gas standard that had  $\text{CH}_4$  and  $\text{N}_2\text{O}$  concentrations close to the atmospheric values ( $1.8 \text{ ppmv}$  and  $0.3 \text{ ppmv}$  of  $\text{CH}_4$  and  $\text{N}_2\text{O}$ , respectively). The air of the laboratory was also sampled regularly in order to correct the concentrations in the sediment. Septum vials were vigorously shaken to equilibrate sediment-water-atmosphere phases. Another set of two cores was used to perform oxygen microprofiles and chlorophyll analysis, and the last set of two cores was taken and sliced at  $1 \text{ cm}$  resolution. One core was used for porosity measurements, and the slices from the second were centrifuged in a nitrogen atmosphere ( $30 \text{ min}$ ,  $9.000 \text{ g}$ , and  $10^\circ \text{ C}$ ). Particulate organic carbon (POC) and nitrogen (PON) were determined in the solid content after acidification with HCl, and the pore water was analyzed for determination of TA, pH, ammonium, nitrate, nitrite, phosphate, silicate, sulfate, calcium, and dissolved organic carbon (DOC).

The water column was well mixed during the samplings; therefore the concentrations analyzed in surface water samples have been used as bottom water values. Samples for determining methane and nitrous oxide concentrations in the water were drawn in  $250 \text{ mL}$  airtight glass bottles, preserved with saturated mercuric chloride to inhibit microbial activity, and sealed with Apiezon® grease to prevent gas exchange. A  $250 \text{ mL}$  airtight glass bottle was filled for TA determination in duplicate (Dickson et al., 2007). Dissolved oxygen (DO) was also measured in duplicate by collecting water in another  $250 \text{ mL}$  airtight glass bottle that was fixed with manganese sulfate (reactive 1) and alkali-iodide-azide (reactive 2) (Hansen, 1999). Frosted stopper glass jars of  $250 \text{ mL}$  were filled up to measure nutrient concentrations in the water column. All samples were stored in the dark until they were analyzed, in duplicate, in the laboratory. *In situ* temperatures were recorded with a mercury thermometer ( $\pm 0.1^\circ \text{ C}$  precision), and salinity was quantified

Download English Version:

<https://daneshyari.com/en/article/8885076>

Download Persian Version:

<https://daneshyari.com/article/8885076>

[Daneshyari.com](https://daneshyari.com)