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In situ oxygen uptake rates by coastal sediments under the influence of the Rhône River (NW Mediterranean Sea)

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ABSTRACT

The influence of riverine inputs on biogeochemical cycling and organic matter recycling in sediments on the continental shelf off the Rhône River mouth (NW Mediterranean Sea) was investigated by measuring sediment oxygen uptake rates using a combination of in situ and laboratory techniques. Four stations were investigated during two cruises in June 2001 and June 2002, with depths ranging from 9 to 192 m and over a distance to the Rhône River mouth ranging from 4 to 36 km. Diffusive oxygen uptake (DOU) rates were determined using an in situ sediment microprofiler and total oxygen uptake (TOU) rates were measured using sediment core incubations. There was good agreement between these two techniques which indicates that the non-diffusive fraction of the oxygen flux was minimal at the investigated stations. DOU rates ranged from 3.7 ± 0.4 mmol O_2 m^{-2} d^{-1} at the continental shelf break to 19.3 ± 0.5 mmol O_2 m^{-2} d^{-1} in front of the Rhône River mouth. Sediment oxygen uptake rates mostly decreased with increasing depth and with distance from the Rhône mouth. The highest oxygen uptake rate was observed at 63 m on the Rhône prodelta, corresponding to intense remineralization of organic matter. This oxygen uptake rate was much larger than expected for the increasing bathymetry, which indicates that biogeochemical cycles and benthic deposition are largely influenced by the Rhône River inputs. This functioning was also supported by the detailed spatial distribution of total organic carbon (TOC), total nitrogen (TN) and C/N atomic ratio in surficial sediments. Sediments of the Rhône prodelta are enriched in organic carbon (2–2.2%) relative to the continental shelf sediments (<1%) and showed C/N ratios exceeding Redfield stoichiometry for fresh marine organic matter. A positive exponential correlation was found between DOU and TOC contents ($r^2=0.98$, $n=4$). South-westward of the Rhône River mouth, sediments contained highly degraded organic matter of both terrestrial and marine origin, due to direct inputs from the Rhône River, sedimentation of marine organic matter and organic material redeposition after resuspension events.

1. Introduction

Continental shelves and coastal areas are among the most productive marine ecosystems (Costanza et al., 1997) and are, consequently, very important regarding our understanding of the organic carbon (OC) cycle (Hedges and Keil, 1995). Because rivers deliver a large amount of dissolved and particulate matter to the continental shelf, they play a key role in benthic biogeochemical cycles of the coastal ocean (Hedges et al., 1997). In river-dominated ocean margins (RiOMar) systems the organic matter cycling is largely driven by dominant processes such as remineralization, storage and reworking that occur in the benthic boundary layer and at the sediment–water interface. Moreover, the rates of primary production, sediment deposition, mineralization and burial in these margins are among the highest of all marine systems and largely influenced by river inputs (McKee et al., 2004).

A key step in the OC cycle is represented by the remineralization of OC at the sediment–water interface via a web of oxidative reactions where the ultimate electron acceptors are O_2, NO_3^-, Mn-oxides, Fe-oxides, SO_4^{2-} and CO_2 (Froelich et al., 1979). The relative importance of the various processes changes with sediment type and sedimentation rate, but generally the oxic mineralization becomes more important with increasing depth (Canfield et al.,

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1993). The majority of the reduced species produced by anaerobic degradation are ultimately reoxidized by an equivalent amount of O_2. Therefore, oxygen uptake rate, integrated over a long time scale, could be used as a proxy of the total benthic carbon mineralization rate, which is a composite of oxic and anoxic mineralization.

Sediment oxygen uptake rate has been widely used to assess benthic OC mineralization during early diagenesis (Glud et al., 1994; Epping and Helder, 1997; Wenzhöfer and Glud, 2002). Total oxygen uptake (TOU) rate can be split into two parts: (i) the diffusive oxygen uptake (DOU) rate, due to sediment bacteria capable of aerobic respiration, and (ii) the advective oxygen uptake rate, generally governed by benthic faunal activities. Several laboratory and in situ techniques have been developed for the quantification of sediment oxygen uptake rates. TOU can be determined in situ with benthic chambers settled on the seafloor (Hall et al., 1989) or ex situ using sediment core incubations (Archer and Devol, 1992). DOU can be quantified by the use of microelectrodes performed in situ or ex situ with sediment cores (Glud et al., 1994).

The Rhône River exerts a large influence on the Gulf of Lions which is the largest RiOMar in the north-western Mediterranean Sea. The influence of the Rhône River inputs on biogeochemical cycles in the Gulf of Lions has been extensively studied (Monaco et al., 1999; Raimbault and Durrieu de Madron, 2003), and is of major importance for biogeochemical cycles. For example, the Rhône River accounts for about 80% of the total river solid discharge to the margin (Durrieu de Madron et al., 2000) and the nutrient inputs are responsible for 50% of the primary production of the Gulf of Lions (Lochet and Leveau, 1990). Regarding the benthic system, most data concerning the Gulf of Lions were compiled in the frame of the EROS 2000 (European River Ocean Systems, 2000) and ECOMARGE program (Ecosystèmes de Marge continentale). The highest sediment oxygen uptake rates were found in front of the Rhône River mouth and decreased offshore (Blackburn, 1993; Helder et al., 1993). More recently, Denis and Grenz (2003) have investigated the TOU distribution in the whole Gulf of Lions using a core incubation technique and they have again emphasized the importance of the Rhône River inputs. Despite these studies, the time and space variability of sediment oxygen uptake rates is poorly documented, particularly for in situ measurements performed in the close vicinity of the Rhône River mouth.

In the present study, oxygen uptake rates were measured in continental shelf sediments located off the Rhône River mouth. Oxygen uptake rates were obtained by two techniques: (i) in situ microelectrodes, which allow the measurements of oxygen profiles and the calculation of DOU rates, and (ii) laboratory core incubations, which provide an estimate of TOU rates. We examined the validity of DOU and TOU estimations and discussed the influence of the Rhône River inputs on the continental shelf sediments. The spatial distribution of organic matter and its characteristics (TOC, TN, C/N ratio) were also examined in order to improve our understanding of geochemical factors that likely control sedimentary mineralization processes.

2. Materials and methods

2.1. Study site

The Gulf of Lions is a large continental shelf located in the north-western Mediterranean Sea along the French coast. The general cyclonic circulation is governed by the north-western Mediterranean current, a seasonal stratification, and aperiodic intense vertical mixing induced by strong regional winds. With a drainage basin of 97 800 km^2 and a mean water flow of 1700 $m^3\,s^{-1}$, the Rhône River is the main source of freshwater, nutrients and organic matter for the Gulf of Lions (Pont et al., 2002), accounting for an annual average supply of particulate OC equal to $1.9 \pm 0.6\,10^5\,t\,yr^{-1}$ (Sempéré et al., 2000). The shape and the extent of the Rhône River plume vary in space and time according to river flow rates and wind regimes (Naudin et al., 1997). The area surrounding the Rhône River mouth is a wide prodelta which accumulates large amounts of terrestrial muddy sediments. In the prodelta, net sedimentation rates range from 30 to 50 $cm\,yr^{-1}$ at the Rhône mouth (Charmasson et al., 1998) and decrease rapidly offshore on the continental shelf, i.e. 0.2–0.6 $cm\,yr^{-1}$ at 20 km away from the outflow (Miralles et al., 2005). Most of the Rhône particulate materials accumulate within the Rhône prodelta, which extends from the shoreline to 60 m depth (Wright and Friedrichs, 2006).

2.2. Field sampling work and elemental analyses

Sediment samples were collected during three different cruises: REMORA 1 (March 2001), PROFILER 2 (June 2001) and MINERCOT 1 (June 2002). Sediment samples were collected with a multicorer Mark VI (Bowers & Connelly) especially designed to simultaneously collect four large diameter Perspex cores (I.D. 15 cm) with an undisturbed sediment–water interface. In March 2001, 24 stations were sampled off the Rhône River mouth (Fig. 1 and Table 1). For each station, 3–5 sub-cores were sliced at 0.4 cm. Then sections from the same depth of each core were pooled and immediately frozen on board for further laboratory analyses: total organic carbon (TOC), total nitrogen (TN) and grain size. In June 2001 and 2002, in situ microelectrode measurements were performed at four stations, following a bathymetric gradient from 9 to 192 m depth (Fig. 1 and Table 1). Fos station is located in the Gulf of Fos and is used as a reference site for coastal sediment studies. Rhône 1 and Rhône 2 stations are directly subjected to the Rhône River inputs. Sofi station is located 36 km away from the Rhône River outflow at a depth of 192 m and is considered a reference site for the continental shelf outside the Rhône River influence. Sediment cores with undisturbed surface structure were also sampled for oxygen incubation in the laboratory, except for Rhône 1 station.

TOC and TN analysis were performed by the CNRS Service Central d'Analyse Elementaire (Vernaison, France) on freeze-dried sediment samples that had been finely powdered and homogenised. Total carbon (TC) concentration was measured with a LECO SC 144 analyser at 1300 °C. Inorganic carbon (IC) concentration was determined with a Shimadzu TOC 5050 combined with a solid sample combustion unit Shimadzu 5000A. The amount TOC was calculated as the difference between TC and IC. TN concentration was determined with an elemental analyser using a procedure, which involved the combustion of sediment at 1050 °C. The nitrogen is converted into nitrogen oxides (NO_x) in a gas flow of He/O_2; the reduction of NO_x by reduced Cu at 600 °C and N_2 determination by catharometry. The average standard deviation of each measurement, determined by replicate analyses of the same sample, was $\pm 0.3\%$ for both TOC and TN and detection limits were 0.3 and 0.07%, respectively. TOC and TN concentrations were expressed as the percentage of sediment dry weight (d.w.).

2.3. In situ microelectrode measurements

We used an in situ benthic microprofiler (Unisense®) equipped with microelectrodes, which allowed the measurement of 5 oxygen and 1 resistivity profiles at the sediment–water interface.