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Organic matter in sediments of a tropical and upwelling influenced region of the Brazilian continental margin (Campos Basin, Rio de Janeiro)

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ABSTRACT

Lipid biomarkers [fatty acids (FAs), sterols and alcohols] and carbon stable isotopes ($\delta^{13}C$ values) in surface sediments from 9 cross shelf transects (25–3000 m water depth) from the Campos Basin, SE Brazilian continental margin were analyzed. The aim was to investigate the link between the prevailing regional specific oceanographic conditions (upwelling events, intrusion of cold and nutrient-rich water, low river input) and the nature and distribution of organic matter (OM) in the basin. A general predominance of OM from autochthonous processes, but with a relevant spatial gradient in the quality and quantity of the sedimentary OM, was observed. On the shelf (<150 m), concentrations of lipids were usually low, except in areas influenced by upwelling, but the presence of labile compounds suggested the occurrence of fresh OM in the sediment. The export of continental OM was observed only in shelf sediments near the Paraíba do Sul River. The upper and middle slope (400–1300 m) exhibited the highest concentrations of total organic carbon (TOC) and lipids, but lipid biomarkers suggested the presence of OM with a high degree of bacterial degradation. This may result from the export of material from shallow areas, possibly due to the action of eddies and meandering of the Brazil Current and bottom currents in the region. On the lower slope (1900–3000 m), only the more recalcitrant compounds were above detection limit. The presence of labile lipids in high amount in the shelf and slope suggests the presence of OM with a high potential for supplying the food requirements of heterotrophic organisms in the sediment, which may in turn have a major influence on the ecology of benthic communities.

1. Introduction

Continental margins are dynamic and complex marine systems where nutrients, sediments, contaminants, energy and biota interact and are transferred in both directions through land-margin and open-margin ocean boundaries, until the deep ocean (Levin et al., 2001; Liu et al., 2010). The extent and magnitude of biogeochemical processes determine the usual enhanced biodiversity observed in continental margin ecosystems (Levin and Sibuet, 2012), but this characteristic is currently threatened by human activity in the coastal ocean and by global change (Bauer et al., 2013; Levin et al., 2015).

The river-estuary-coastal ocean continuum provides the major pathways for transferring carbon among environmental compartments, although the magnitude and mechanisms of the processes involved are yet to be constrained in detail (Jahnke, 2009; Bauer et al., 2013). Current estimates of continental margin contribution to the global primary production and carbon burial in sediments amount 10 to 30% and >40–80%, respectively (Hedges and Keil, 1995; Liu et al., 2010; Bao et al., 2016). The identification of the labile and detrital pools of OM is important, as the balance between these two types of OM has an influence on the long term accumulation of C in sediments (Pearson et al., 2001) and the quality rather than the quantity of OM is an important driver of benthic ecology (Pusceddu et al., 2009).

A wide range of geochemical indicators is usually necessary for investigating OM biogeochemistry in aquatic systems due to the diversity of sources and complexity of the processes involved. They can be broadly divided into molecular and isotopic categories. The appropriate choice of such proxies allows inferences about the relative contributions of autochthonous and allochthonous sources, and the identification of the main processes responsible for the transport, transformation and accumulation of OM in aquatic environments (Volkman, 2006; Bianchi and Canuel, 2011). Lipid biomarkers are commonly used as molecular indicators because vegetation and animal metabolisms produce functionally specific compounds which can be assigned to distinct sources of OM (bacterial, plankton, riverine and/or terrestrial) and that can persist in the environment over a range of historical and/or geological

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timescales. Regarding isotopes, the fractionation (i.e. discrimination against the heavy isotope) caused by kinetic or thermodynamic factors results in specific isotopic signatures of the bulk OM according to its source (Hoefs, 2009). In the case of carbon, there are differences in the $^{13}C/^{12}C$ ratio depending on the carbon metabolism in higher plants (via C_3, C_4 or CAM pathways), environmental factors like temperature, pH and concentration of CO_2 and the isotopic composition of inorganic C used for terrestrial (atmospheric air) or water (dissolved gas) plants during photosynthesis (Macko et al., 1993; Popp et al., 1998).

Here we focus on the Campos Basin (20–24°S and 39–42°W), on the SE Brazilian continental margin (SEBCM), a region of economic (petroleum, fisheries) and ecological significance. The major oceanographic features in the region are a low river input and coastal and shelf upwelling of cold, nutrient-rich South Atlantic Central Water (SACW). These events are enhanced during austral spring and summer seasons under prevailing NE winds on the Cabo Frio coast (23°S/42°W), but also can occur intermittently all year round and reach hundreds of miles on the platform (Valentin et al., 1987; Lorenzzetti and Gaeta, 1996; Campos et al., 2000; Castelao and Barth, 2006). The upwelling plumes have great influence on the pelagic and benthic production of autotrophic and heterotrophic organisms (Valentin et al., 1986; Gonzalez-Rodriguez et al., 1992; Sumida et al., 2005; De Leo and Pires-Vanin, 2006; McManus et al., 2007; Guenther et al., 2008; Yoshinaga et al., 2008). In recent years, foraminifera and inorganic chemical proxies from surface and core sediments have been applied to investigate biogeochemical processes specific to the Cabo Frio upwelling system (Albuquerque et al., 2014, 2016; de Oliveira Lessa et al., 2014; Sanders et al., 2014; Venancio et al., 2014, 2016; Lessa et al., 2016). However, a basin-scale assessment of the quality and quantity of OM in the SE Brazilian continental margin is lacking, with most studies relatively limited in spatial resolution (Sumida et al., 2005; Yoshinaga et al., 2008; Carreira et al., 2010; Oliveira et al., 2013; Sanders et al., 2014).

The present study therefore aimed to investigate the processes related to the origin, transport and accumulation of OM in surface sediments of the Campos Basin on a regional scale, in order to increase understanding of the ecological relationships between the nature and composition of OM and the structure of the benthic food chain in the region. To achieve this, a range of geochemical indicators was considered – total organic carbon (TOC) content, carbon isotopic composition ($\delta^{13}C$) and molecular markers (*n*-alcohols, sterols and fatty acids, FAs) – in 215 sediment samples collected on two sampling occasions from 9 transects along 12 isobaths ranging from 25 m to 3000 m water depth.

2. Material and methods

2.1. Sampling procedure

The study is part of a larger project (“Habitats Project – Campos Basin Environmental Heterogeneity”) designed, coordinated and funded by the research center (CENPES) of Petrobras, the Brazilian energy company. In order to obtain a wide coverage of the Campos Basin area, sampling occurred at 108 stations along 12 isobaths (25, 50, 75, 100, 150, 400, 700, 1000, 1300, 1900, 2500 and 3000 m) and 9 transects, A to I (Fig. 1). Sampling stations were positioned to avoid areas with oil platforms, pipelines and wells as well as the presence of submarine canyons. Because the 2 cm internal was larger than rate of accumulation between seasons, the two samplings were viewed as “snapshots” of the systems and comparisons of the seasons was not explored. Samples were collected in two periods – winter of 2008 (dry season) and summer of 2009 (wet season), aboard the R/Vs Gyre and Emma McCall. A box corer and a large grab (230 l) were used for sampling and, onboard, the undisturbed upper 2 cm of the sedimentary column were subsampled by inserting a metal tube. Samples were collected at each station using three independent deployments of the sampler. The replicate samples were stored at −20 °C, freeze-dried in the laboratory and then homogenized to create a single composite sample. A total of 215 homogenized samples were analyzed.

2.2. Elemental analysis and isotopic analysis

TOC and total nitrogen (TN) were determined using a Carlo Erba EA 1110 elemental analyzer after removal of inorganic carbon with 0.1 mol/l HCl (Hedges and Stern, 1984). Sub-samples (8–10 mg) of ground and carbonate-free sediment were weighed (precision ±0.01 mg) in Sn containers, folded and placed in the instrument. Quantification was performed based on the instrument response relative to a standard (cysteine). Analytical precision was estimated as 3% or better for TOC and TN (based on 4 replicate analyses of the same sample) and accuracy was verified by analyzing a reference material (PACS-2, National Research Council of Canada). TOC data are given relative to bulk sediment, i.e. they were corrected for sample carbonate content.

The sediments for isotopic analysis (10–15 ± 0.01 mg) were acidified and kept overnight in HCl 1 mol/l before drying. The carbonate-free residue was converted to CO_2 and N_2 in a Thermo Flash EA Elemental Analyzer and the gases formed directly injected in a Thermo Delta Plus stable isotope ratio mass spectrometer. The carbon isotopic composition is expressed as $\delta^{13}C = [R_{sample}/R_{standard}-1]$, where R is the ratio of the heavy isotope to the light isotope ($^{13}C/^{12}C$). For instrument calibration, CO_2 from a cylinder previously calibrated in relation to the USGS40 (L-glutamic acid) standard was used. The reproducibility of the measurement was typically better than ±0.2‰. The N isotopic composition was not measured, so no data are reported here.

2.3. Lipid analysis

Lipids (FAs, sterols and alcohols) were quantified following the method described by Carreira et al. (2015). In brief, ca. 5.0 g (precision ±0.01 g) of freeze-dried sediment were extracted with dichloromethane (DCM)/MeOH (9:1, v:v) in a Soxhlet apparatus for 24 h, after addition of surrogate standards [5α-androstan-3β-ol, C_{19} and C_{21} FA methyl esters (FAMES) and nonadecanol]. Extracts were saponified (1M KOH at 110 °C for 2 h) and the neutral lipids (sterols and alcohols) recovered with *n*-hexane and further purified using column chromatography with activated silica gel. Assignment and quantification of sterols and alcohols (as trimethylsilyl ethers) were performed using gas chromatography-mass spectrometry (GC-MS; Thermo Focus DSQ). Quantification was performed using a calibration curve with commercial standards and by considering the peak areas of key ions (*m/z* 129 or 215 for sterols and *m/z* 103 for *n*-alcohols and phytol) and response factors relative to the internal standard (5α-cholestane, *m/z* 217). Similar response factors for key ions were assumed for structurally related compounds for which standards were not commercially available.

The acidic lipids (FAs) were recovered from the saponified extract with *n*-hexane after acidification to pH < 2 and then methylated (BF_3/MeOH at 85 °C for 2 h) without further purification. Analysis of FAMEs was performed by way of GC with flame ionization detection (FID; Hewlett-Packard 6890), whereas confirmatory analysis was performed by way of GC-MS of selected samples. FAMEs were assigned and quantified using a calibration curve prepared with a standard (C_{37} FAME, Supelco®) and deuterated tetracosane as internal standard. Mean quantification limit (QL) for lipids was 0.03 μg/g. Mean recovery of surrogates was 80 ± 24% and 76 ± 21% for C_{19} and C_{21} FAMEs (for FAs), respectively,