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Baseline

Characterization of organic matter in sediment cores of the Todos os Santos Bay, Bahia, Brazil, by elemental analysis and ^{13}C NMR

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ABSTRACT

The impact of human activity on the sediments of Todos os Santos Bay in Brazil was evaluated by elemental analysis and ^{13}C Nuclear Magnetic Resonance (^{13}C NMR). This article reports a study of six sediment cores collected at different depths and regions of Todos os Santos Bay. The elemental profiles of cores collected on the eastern side of Frades Island suggest an abrupt change in the sedimentation regime. Autoregressive Integrated Moving Average (ARIMA) analysis corroborates this result. The range of depths of the cores corresponds to about 50 years ago, coinciding with the implantation of major onshore industrial projects in the region. Principal Component Analysis of the ^{13}C NMR spectra clearly differentiates sediment samples closer to the Subaé estuary, which have high contents of terrestrial organic matter, from those closer to a local oil refinery. The results presented in this article illustrate several important aspects of environmental impact of human activity on this bay.

1. Introduction

The chemical composition of sedimentary organic matter may vary with climate, proximity to the shore and the relative contributions of marine and continental organic matter residues. Anthropic influence on the environment modifies the composition and concentration of the organic matter, potentially affecting the local biota. Carbon and nitrogen are the two main components of the organic matter. The organic carbon content in surface sediment depends on a series of factors such as sedimentary characteristics, rate of microbial degradation, water column productivity and proportion of terrestrial inputs. Organic matter from higher plants has low nitrogen content and thus a high carbon/nitrogen (C/N) ratio. Therefore, higher C/N ratios in marine sediments indicate a predominantly terrestrial source of organic matter, whereas sediments rich in marine organic matter have lower C/N ratios (Burone et al., 2003). According to Bordovsky (1965), marine sediments near river exhibit the highest C/N ratios, indicating the input of terrestrial material into the area. The input of inorganic nitrogen by sewage can contribute to lowering the C/N ratio.

Solid-state ^{13}C NMR spectroscopy provides techniques that enable reliable identification of insoluble sediment organic structures (Patience and Wilson, 1990). To achieve a high sensitivity in this task, a combination of ^{1}H–^{13}C cross-polarization with radio-frequency ramp (ramped-CP), magic-angle spinning (MAS) and high power ^{1}H dipolar decoupling (DEC) is normally used (Peersen et al., 1993). The ^{13}C ramped-CP/MAS method allows carbons associated with distinct molecular groups, such as alkyl, methoxyl, O-alkyl, di-O-alkyl, aromatic, and carboxyl (Hedges and Oades, 1997), to be distinguished in the organic fraction of marine sediment.

The sedimentation regime in Todos os Santos Bay has undergone many important changes due to the impact of human activities. The sediment cores studied in this article were collected in the northern part of the bay, three in the clayey region near the harbor of Madre de Deus and the Mataripe Refinery, where many oil refining and transport operation are concentrated, and three near the estuary of the Subaé River and the old oil-drilling extraction field, Dom João.

In this article, a set of experimental data obtained by various techniques are reported and analyzed statistically, to estimate the impact of human activity on this bay.

2. Materials and methods

2.1. Study site

Todos os Santos Bay, Bahia, is the largest Brazilian bay, with an area of 1086 km^2. It is located between west longitudes 38°25' and

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38°45', and south latitudes 12°35' and 13°00' (Fig 1). The sites investigated are located at the northern end part of the Bay, where the dominant material in the sediments is a very fine mud. Mangroves and the estuaries of rivers characterize the coastline in this region.

2.2. Sampling

The sediments were sampled by one core at each site (T1, T2, T3, T4, T5, and T6), as illustrated in Fig. 1. The first set of cores (T1, T2, and T3) was collected from three sites in the vicinity of the Mataripe refinery and Madre de Deus harbor, to the east of Frades Island. The other three sites (T4, T5, and T6) were located west of Frades Island, close to the Subaé River estuary (Fig. 1). These sites were chosen for their proximity to industrial activities and the influence of the Subaé (main) and Paraguaçu rivers. The core samples were collected manually by inserting a tube, about 1 m long and 0.075 m in diameter, into the sediment. The water depth over the sampling sites varied between 2 and 10 m. The cores were maintained at 0 °C in the boat and in transit and at −20 °C in the laboratory. They were cut into 2.5-cm sections; freeze dried and stored at −20 °C until analyzed.

2.3. Elemental analysis

The determination of total organic carbon (TOC), nitrogen (N), and sulfur (S) was carried out in carbonate-free sediment samples treated with 10 mL of 1 M hydrochloric acid (Ryba and Burgess, 2002 and Burone et al., 2003). Portions of each sample (15–20 mg) were weighed in small tin capsules and analyzed in a CHNS Thermo Finnigan Flash EA 1112 series elemental analyser. The calibration was verified by measuring samples of certified reference marine sediment NIST 1941b, treated in the same way as the samples.

Because of the characteristics of depth sampling, the longitudinal data analysis approach was adopted, using an Autoregressive Integrated Moving Average (ARIMA) model with a gradual permanent impact, in order to model the anthropic impact, 50 years ago, through the alteration in the sediment composition. This model takes autocorrelation into account and has the following fitting parameters: the initial value (intercept); the statistical significance of the intervention, in this case the implementation of a refinery; the rate of alteration due to the intervention (ω); the time taken for the new level to be stabilized (δ) and the asymptotic change, i.e. the increase/decrease of the initial level after the series is stabilized.

After the stationary state, the ARIMA model was adjusted for each analyzed element (C, N, and S) and for the ratios C/N and C/S. All the adjustments were performed with only one autoregressive parameter – ARIMA (1,0,0). The adjusted parameters (intercept, final value, δ, ω, and asymptotic change) of the sites were compared in pairs by Student's *t*-test at a 5% level of significance. The variance homogeneity was assessed by the *F* test and, according to the results, the appropriate *t*-value was used.

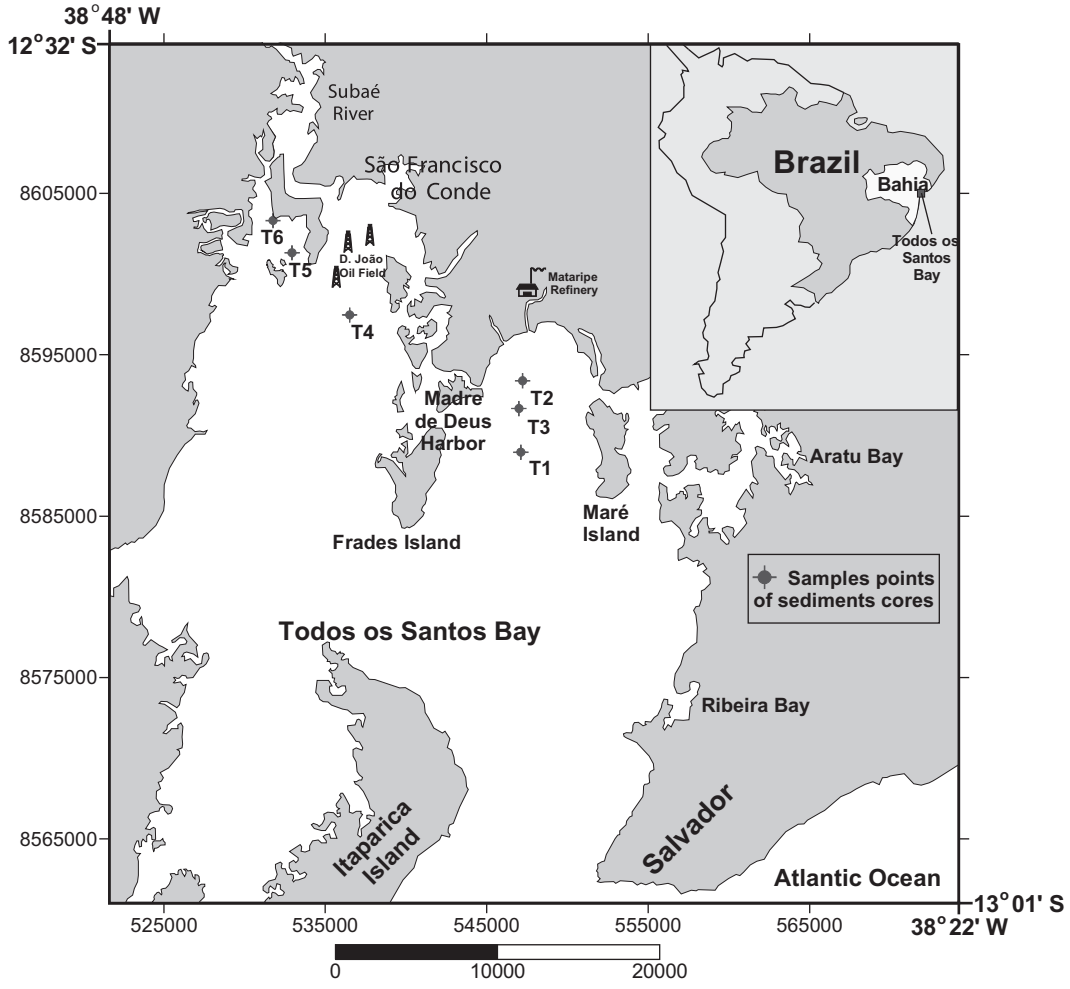

Fig. 1. Todos os Santos Bay map with sediments cores localization.