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# Characterization of organic matter in a sediment Core near the Mataripe refinery, Bahia–Brazil



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### ABSTRACT

A sediment core was taken from the Todos os Santos Bay, near the Mataripe Bahia-Brazil refinery. The results of dating, <sup>210</sup>Pb and <sup>137</sup>Cs methods, combined with organic indicators, Polycyclic aromatic hydrocarbons (PAHs), *n*-alkanes and total organic carbon (TOC), showed significant change with the start of production of the oil fields of Aratu, Itaparica and Dom João (1939-1947) and the construction of the Mataripe refinery (1949-1950). This event was marked by a series of significant changes, including an abrupt increase in TOC and the growth of PAH concentrations and the presence Unresolved/Resolved ratio (UR/R) > 4 in *n*-alkanes fraction, which indicated that the contamination was of petrogenic origin.

The  $\delta^{13}$ C of specific *n*-alkanes compounds showed gradual deplete with the depth.

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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 (Costa et al., 2011). This process maintains a vital connection between the redox processes and the food chain (Deshmukh et al., 2001). However, human influence alters the composition and concentration of organic matter, which may affect the local biota. There is a large array of organic compounds, but because of their large usage and potential adverse effects, the polycyclic aromatic hydrocarbons (PAHs) deserve special attention. Hydrocarbons are good tracers for determining the source of organic matter in sediments (Meyers, 2003; Asia et al., 2009). Waxes of terrestrial plants, phytoplankton, and bacteria are among the possible sources of naturally occurring hydrocarbons. The burning of fossil fuels, municipal and industrial effluents and accidents in the transport and storage of oil and its derivatives are among the possible anthropogenic sources of hydrocarbons (Gogou et al., 2000). Aliphatic hydrocarbons and PAHs are the main components of crude oil, which is one of the main pollutants in coastal areas that contribute to the degradation of the environment (Gao and Chen, 2008; Hostettler et al., 1999; Page et al., 1996; Wu et al., 2001; Yunker et al., 1993). Oil contamination is frequently determined by using the isotopic ratios of oil derivative (Meyer-Augenstein, 1999; Philp et al., 2002). Isotopic fractionation, which is a process that discriminates heavy isotopes from light isotopes (Boutton et al., 1996; Meyers, 2003), allows for the identification of specific compounds when an analysis by *n*-alkanes is not sufficient to discriminate sources (Sikes, 2009).

To estimate the severity of the contamination due to oil (petrogenic), Volkman et al. (1992) proposed some indicators: i) high

concentrations of total hydrocarbons (>100  $\mu$ g/g of dry sediment); ii) *n*-alkanes having no odd over even predominance; iii) complex distributions; iv) an unresolved complex mixture (UCM), which produces a "ramp" on the baseline in the gas chromatogram of the hydrocarbon fraction; and v) biomarkers. In general, the UCM is considered a very complex mixture of structural isomers and homologues of branched and cyclic hydrocarbons that cannot be resolved by a capillary column gas chromatograph.

This study aimed to infer the history of anthropogenic contribution to organic matter from marine sediments of a dated sediment core, which was located in a centre of great human activity in the Todos os Santos Bay (TSB), by analysing the behavioural characteristics of organic compounds that occurred along the sediment core. The results related these variations with the onset of increased human activity in the vicinity of the bay.

The TSB is one of the largest bays in Brazil, covering 1086 km<sup>2</sup> with an average depth of 6 m and reaching depths of up to 102 m (Argollo, 2001). The TSB is characterized as a fluvial-marine depositional environment with strong human influences that are associated with heavy and disorderly occupation, industrialization, port and gas/oil activities. The TSB includes the first exploration site for petroleum in Brazil. The daily production was approximately 2.5 thousand barrels per day in 1950, when a refinery was first constructed (Landulpho Mataripe Alves refinery - RLAM). Although oil exploration decreased significantly since that time, the petroleum industry developed, and today, it represents the largest petrochemical complex in the southern hemisphere. The study site (Fig. 1) was located in the northern part of the TSB in the region between the cities of Madre de Deus and São Francisco do



Baseline

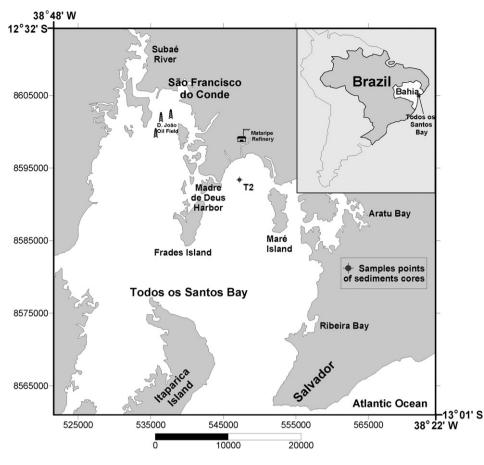


Fig. 1. Location of core (T2) collection at Todos os Santos Bay, Bahia.

Conde. In this region, the sediments were mainly composed of mud (Argollo, 2001).

An approximately 1-m-long sediment core (Fig. 1) was collected with the help of divers, in the region near RLAM in August 2002. Immediately after collection, the core was sealed with a high-density polyethylene cap and stored upright in a container filled with ice. The core was frozen immediately upon arrival at the laboratory. The sediment core was then sliced and freeze-dried for analysis. The models of Krishnaswami et al. (1971) and Robbins et al. (1978) were used for the analysis. The method was based on the radioactive decay of <sup>210</sup>Pb excess, simple model, and the <sup>137</sup>Cs content was detected to check the sediments deposited during the period 1964–1965 (Hermanson, 1990; Argollo, 2001). The excess of <sup>210</sup>Pb was calculated as the difference between the activities of the total <sup>210</sup>Pb and <sup>226</sup>Ra present in the sediment.

For the analysis, 9 g–12 g of sediment was placed in polyethylene containers, which were sealed to prevent the escape of <sup>222</sup>Rn formed

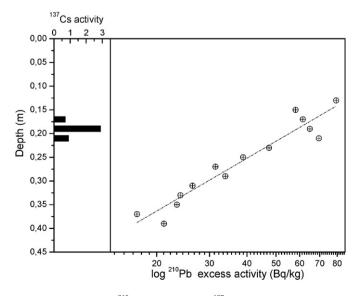


Fig. 2. Variation of <sup>210</sup>Pb excess activity and <sup>137</sup>Cs activities with depth.

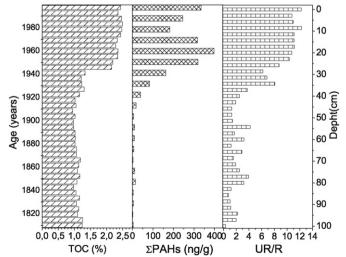


Fig. 3. Dated profiles of TOC,  $\sum$  PAHs and ratio of aliphatic components unresolved by solved.

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