



## Baseline

## Mercury deposition during the previous century in an upwelling region; Cabo Frio, Brazil



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## ABSTRACT

To investigate the upwelling influence on Hg biogeochemical cycles and the sedimentological changes during the previous ~150 years, four sediment box-cores were sampled along an inshore offshore transect on the Southeastern Brazilian continental shelf. Mercury values were found to be relatively low, with means ranging between 8.08 and 30.4 ng g<sup>-1</sup>. Mercury fluxes along the sediment cores are directly related to the well documented historical regional activity and global atmospheric deposition. The narrow relationship between mercury and organic carbon suggest that upwelling phenomenon and primary production may play an important role on Hg input and distribution along continental shelf depositional settings.

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Mercury has been anthropogenically emitted for several millennia, first from pre-industrial gold and silver mining (Nriagu, 1994; Hylander and Meili, 2003) and subsequently as a result of global industrial growth in early twentieth century (Biester et al., 2007; Yang et al., 2010). Mercury can be transported over great distance because of its atmospheric residence time of 1–2 years (Morel et al., 1998; Lin and Pehkonen, 1999). It is well known that Hg has unique geochemical characteristics such as a strong affinity to organic matter and redox sensitivity, often indicated by Mn an Fe behavior (Sanders et al., 2008; Gehrke et al., 2009). Such characteristics make Hg strongly cyclical and embedded in the food chain (Ullrich et al., 2001). Knowledge of the kinetic processes, in many cases causing enrichment, is increasingly used as indicators of environmental changes (Morford and Emerson, 1999; Nameroff et al., 2002; Tribouillard et al., 2006; Sanders et al., 2006; Mohtadi et al., 2008).

Overall, the amount of Hg emitted from land, oceans and anthropogenic sources (burning coal, mining for various metal and industrial activities that process ore and/or produce cement) may reach ~7.0 Kt y<sup>-1</sup> (Mason and Sheu, 2002; Selin et al., 2010). From this quantity, the oceans are responsible for emitting 2.8 Kt y<sup>-1</sup> (Selin et al., 2010). However, 3.08 return through atmospheric deposition and only 0.68 Kt y<sup>-1</sup> are immobilized in sediments (Mason and Sheu, 2002). Therefore, oceans play an important role in the global Hg cycle; serving both as a source, as well as a sink for atmosphere derived Hg (Mason et al., 1994; Mason et al., 2001).

Continental shelves are important biogeochemical interfaces between land and ocean. These systems occupy only 8% of the oceans yet are responsible for 25% of global primary productivity (Knoppers et al., 2009). The high primary production in these regions is influenced by rivers and atmospheric inputs, remineralization of benthic–pelagic and upwelling of nutrients (Martinez et al., 1999; Knoppers et al., 2009).

Upwelling enhances the supply of reactive inorganic Hg species, through lateral transport to coastal waters, which may adhere to organic matter (Mason and Fitzgerald, 1991; Mason and Sullivan, 1999; Silva et al., 2001; Laurier et al., 2004; Cossa et al., 2004). Both sediment focusing and boundary scavenging represent lateral transport. Sediment focusing is the transport of particle reactive tracers already attached to particles, while boundary scavenging is where the dissolved Hg is supplied to sinking particles or supplied to deposited sediments in the dissolved form. As a result of upwelling and subsequent eddies, lateral transport along continental shelves may be important in site specific Hg enrichment.

There are few studies addressing sedimentary Hg biogeochemistry in upwelling zones, and the role of Hg deposition to marine sediments is still unknown. In this study we examine and discuss Hg input during the previous century to the continental shelf sediments in Southeastern Brazil. The objective of this work is to shed light on how highly productive upwelling systems have an effect on Hg deposition. Because of the large amount of organic matter deposited on the Cabo Frio upwelling region, we hypothesize that Hg is also being deposited in specific areas of the continental shelf.

Sampling procedures and site description are discussed in Diaz et al. (2012). Sediment density was determined through a gamma density system with 0.5 cm resolution (Multi-Sensor Core Logger

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– MSCL-GEOTEK). The grain-size analysis was performed in a CLAS mod. 1064 laser analyzer after each sample was treated with 1N HCl in order to remove calcium carbonate and extended peroxidation to remove organic matter. Each sample was disaggregated with sodium hexametaphosphate 4% (Loring and Rantala, 1992). Total organic carbon (TOC), C/N ratio,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  were performed through EA/IRMS (PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer) at the UC Davis Stable Isotope Facility, USA. Sediment geochronology was determined through the  $^{210}\text{Pb}$  and  $^{239+240}\text{Pu}$  dating methods, well described in Sanders et al., 2010. For Hg content, 2 g of freeze dried sediment were weighed and digested in 50% aqua regia for one hour at 70 °C in a closed system (Malm et al., 1989). Mercury was analyzed by CVAAS (Cold Vapor Atomic Absorption Spectrometry) in a Bacharach Coleman-50D mercury analyzer system after Hg (II) reduction through  $\text{SnCl}_2$ . Simultaneous determination of Hg in reference standards (PACS-2, NRCC) was performed using the same analytical procedure. Analytical precision and accuracy were better than 6%. Iron and Mn were analyzed following a modification of the U.S. EPA Method 3051. 0.2 g of lyophilized sediment was weight and extracted by closed-vessel microwave digestion on Berghof (Speed wave) with  $\text{HNO}_3$  concentrate. The extracts were analyzed by AAS (Spectrometry Atomic Absorption, Varian, AA 2402). Simultaneous determinations of Fe and Mn in reference standards (PACS-2, NRCC) were performed using the same analytical procedure, and the recovery of Fe and Mn was respectively 88.26% and 82%. S total (%) values were obtained from Diaz et al. (2012).

The silt-clay fraction was predominant in the four cores collected, the highest and lowest values were observed in the central portion of the shelf (BCCF10-04 and BCCF10-09) and both extremities of a mud bank which is the outlined area in Fig. 1 (BCCF10-01 and BCCF10-15) (Table 1). No significant differences were observed between the BCCF10-01 BCCF10-15 cores regarding the content of silt- ( $p > 0.05$ , Mann-Whitney U test), the same was observed for the cores located in the central portion of the mud bank ( $p > 0.05$ , Mann-Whitney U test) (Fig. 2B and C).

Total organic carbon content ranged from 0.7% to 2.7%, with an average value of approximately 2% for the entire survey area. These contents were similar to those found in Oman upwelling zone (Passier et al., 1997; Sirocko et al., 2000) and Indian Ocean upwelling (Baumgart et al., 2010). The highest OC contents were in the

BCCF10-04 and BCCF10-09 core (Table 1), though TOC did not vary significant between cores ( $p > 0.05$ , Mann-Whitney U test).

The C/N molar ratios in this study ranged from 6.78 to 9.95, which varied slightly between the four cores. The  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  ranged from  $-22.38$  to  $-20.98\text{‰}$  and 3.07 to 7.36‰, respectively. The values found in this work indicate a dominant marine source of the OC deposition to the study area, likely influence by the high primary productivity in the region.

From the  $^{210}\text{Pb}$  and  $^{239+240}\text{Pu}$  calculated sedimentation rates (SR), profiles shown in the Supplementary material, sediment core ages were determined (Table 1). The SR was higher in BCCF10-15 ( $0.55 \text{ cm y}^{-1}$ ) with a gradual decrease toward the outer shelf ( $0.10 \text{ cm y}^{-1}$ ) (Table 1). The values obtained in the core BCC10-01-04 and BCCF10 BCCF10-09, SR are comparable to other upwelling systems in the world, such as the northeast African coast ( $\approx 0.21 \text{ cm y}^{-1}$ ) (Mcgregor and Mulitza, 2007) and the continental margin of Peru and Chile ( $0.04\text{--}0.29 \text{ cm y}^{-1}$ ) (Muñoz et al., 2004).

Mercury contents in surface sediments (0–2 cm) ranged from 2.60 to 37.45  $\text{ng g}^{-1}$ . These contents are higher than the background values reported for Brazilian southeastern shore ( $15\text{--}30 \text{ ng g}^{-1}$ ) (Marins et al., 2004). Indeed, the concentrations in this work are similar to those found in depth sediments from Campos Basin, situated north of the study area ( $8\text{--}35 \text{ ng g}^{-1}$  north portion and  $8\text{--}29 \text{ ng g}^{-1}$  south portion) (Araújo et al., 2010). However, the Hg content in the Cabo Frio sediments reached higher values, which may be explained by the physical characteristics of the sediments in both areas. The Cabo Frio sediments were sampled over a muddy bank, where the silt-clay percentage reached values higher than Campos Basin (silt-clay fraction 72–81%). Furthermore, the organic carbon in the Cabo Frio region are higher than values found for Araújo et al. (2010), which may favor greater Hg accumulation in the sediments of this region.

In the BCCF10-01, BCCF10-04 and BCCF10-15 sediment cores, the Hg content did not contain significant statistical correlation with other parameters (Table 3). However, in the BCCF10-09 core, Hg was significantly correlated with the Mn along the entire profile (Spearman = 0.76,  $p < 0.05$ ). This same geochemical pattern was observed by Asmund and Nielsen (2000) in Arctic marine sediments. Asmund and Nielsen (2000) provide evidence to support that the Mn redox cycle directly influences the Hg remobilization/precipitation in oxidizing sediments. In this word, the weak fluctuations in Fe and Mn concentrations (Table 2) and the

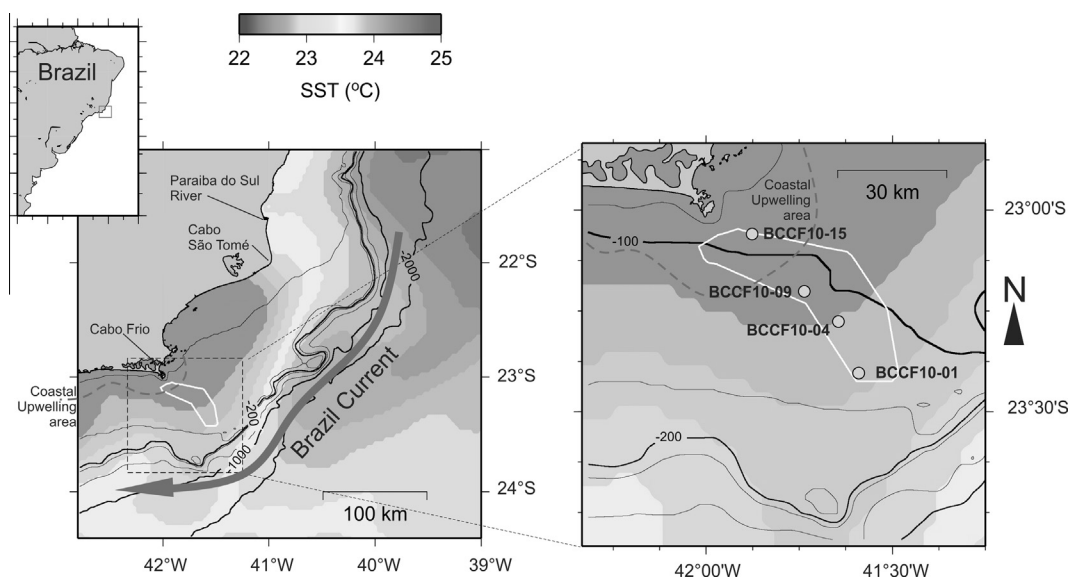


Fig. 1. Location of the study area and sampling sites.

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