



## 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 and 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 CILAS 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

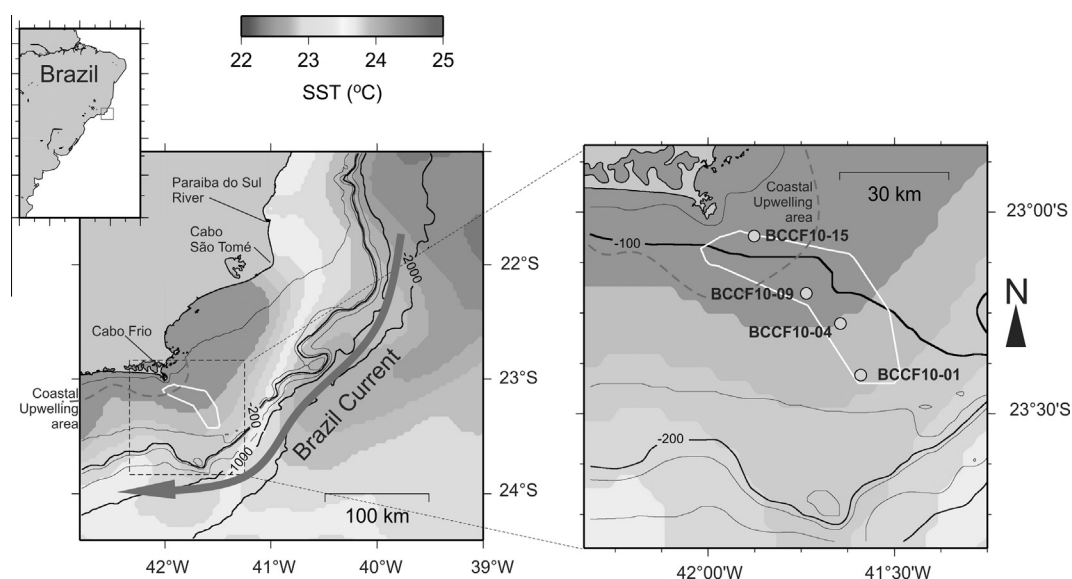
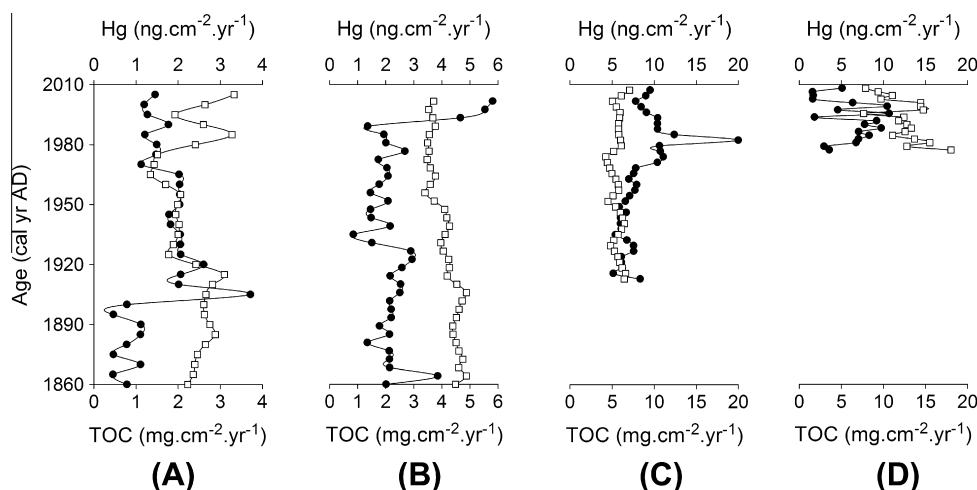


Fig. 1. Location of the study area and sampling sites.

**Table 1**

Mean characteristics of sediments from four box-cores collected on the Cabo Frio continental shelf. Depth (water depth in m); Length (core length cm); SAR (sediment accumulation rate in  $\text{cm yr}^{-1}$ ); Density ( $\text{g cm}^{-3}$ ); TOC (total organic carbon  $\text{mg g}^{-1}$ ); age (years).

Core	Lat (S)	Long (W)	Depth	Length	SAR	Density	Silt-clay (%)	TOC	Age
BCCF10-01	23°40'39,00"	−41°59'00,00"	128	15	0.10	$1.65 \pm 0.02$	$58.7 \pm 10.3$	$13.8 \pm 3.30$	150
BCCF10-04	23°28'03,99"	−42°04'47,00"	120	18	0.14	$1.63 \pm 0.08$	$89.5 \pm 8.30$	$20.8 \pm 1.70$	150
BCCF10-09	23°20'13,99"	−42°14'01,00"	117	17.5	0.18	$1.54 \pm 0.09$	$92.3 \pm 6.0$	$19.1 \pm 3.34$	97
BCCF10-15	23°06'25,99"	−42°28'01,00"	79	18	0.55	$1.29 \pm 0.15$	$61.1 \pm 12.2$	$17.4 \pm 3.0$	33



**Fig. 2.** Hg fluxes along the continental shelf from the cores collected on the Cabo Frio continental shelf. The black circles represent the Hg, while the white square represents TOC. (A) BCCF10-01, (B) BCCF10-04, (C) BCCF10-09 and (D) BCCF10-15.

significant correlations between them in the BCCF10-01, BCCF10-04 and BCCF10-15 cores (Table 3) suggest that there are not major changes in redox conditions along the sediment column, indicating that the Hg bonds are not preserved due to other post-depositional geochemical processes.

The geochemistry of Hg in the sediments is chiefly controlled by both quantity and quality of organic matter (Hammerschmidt and Fitzgerald, 2004; Hammerschmidt and Fitzgerald, 2006). Gehrke et al. (2009) showed in western Mediterranean that an increase of Hg in sedimentary layers correlated with high contents of organic carbon (0.95–4.52%). The authors demonstrated that the concentrations of this metal was correlated to high productivity, which likely altered the redox conditions, favoring the preservation of Hg within the sediment column. However, our results show that this does not apply to Cabo Frio region due to the following reasons:

Because the Cabo Frio continental shelf is marked by complex hydrodynamics, formed by displacement of different water masses, oxidizing conditions are favored in bottom sediments. This hypothesis is supported by recent studies about the geochemistry of sedimentary sulfur in the same sediments of the Cabo Frio continental shelf (Diaz et al., 2012). Monosulfide (AVS) values were below detection limits and very low levels of pyrite sulfur (CRS) exist (0.05–0.3 wt%), suggesting a low rate of sulfate reduction and oxidizing conditions (Diaz et al., 2012).

The dynamic hydrodynamic conditions in the Cabo Frio continental shelf result in differing depositional patterns (Mahiques et al., 2002). To attempt in better understanding the Hg depositional conditions of the study area, through a chronological model which considers the accumulation rate, may be determined according to the equation:  $\text{Hg AR} = [\text{Hg}] \cdot \text{SR} \cdot \rho$ ; where  $[\text{Hg}]$  is the measured Hg concentration in each layer, SR is the sedimentation rate;  $\rho$  is the density of the sediment found in each layer.

The highest average fluxes of Hg were found in cores BCCF10-09 and BCCF10-15 (Table 3). These results indicate the influence of depositional processes on Hg accumulation in this area. Indeed,

**Table 2**

Mean concentrations of Hg, Fe, Mn and total S at the four box-cores from Cabo Frio continental shelf.

Cores	Hg ( $\text{ng g}^{-1}$ )	Fe ( $\text{mg g}^{-1}$ )	Mn ( $\text{mg g}^{-1}$ )	S total%
BCCF10-P1	$9.34 \pm 4.23$	$3.77 \pm 0.21$	$0.13 \pm 0.004$	$0.14 \pm 0.05$
BCCF10-P4	$11.7 \pm 5.58$	$5.21 \pm 0.31$	$0.18 \pm 0.009$	$0.22 \pm 0.04$
BCCF10-P9	$30.4 \pm 11.1$	$7.53 \pm 0.31$	$0.20 \pm 0.014$	$0.26 \pm 0.03$
BCCF10-P15	$8.08 \pm 4.43$	$4.21 \pm 0.15$	$0.16 \pm 0.01$	$0.20 \pm 0.04$

in the BCCF10-09 core, the mean Hg flux was near four times greater than in the core BCCF10-04 and 8 times higher than in core BCCF10-01. Furthermore, core BCCF10-09 has a concentration peak two times larger than core BCCF10-15. These results show a clear existence of other factors that act on the depositional processes of Hg in the region.

The presence of meanders, cyclonic and anticyclonic eddies in the middle portion of the Cabo Frio continental shelf can create upward and downward movements as well as lateral transport of water masses (Mahiques et al., 2005). Thus, the type and amount of material transported to the seafloor are associated with the oceanographic forcing in the region. These phenomena explain the large accumulation of fine sediments in the middle shelf.

Mercury accumulation rates show a trend of enrichment in the middle shelf cores (BCCF10-04 and 09) (Fig. 2). The results in this work corroborate with the studies in southeastern Brazil, where Hg accumulation rates reached maximum values ( $4\text{--}10 \text{ ng cm}^{-2} \cdot \text{yr}^{-1}$ ) between 1940 and 1960 (Lacerda and Ribeiro, 2004). However, Lacerda and Ribeiro (2004) observed a fast Hg accumulation between the 70s and 80s, which may be noted in the middle shelf cores (BCCF10-09), where the Hg deposition reached its highest values (Fig. 2), approximately two times higher than the values found by Lacerda and Ribeiro (2004) in this same period. This peak is explained by large quantities of Hg imported to Brazil between the 70s and 80s ( $160 \text{ t yr}^{-1}$ ) reaching 340 t in 1989. Most of the

**Table 3**

Spearman correlation coefficients for each sediment core. Significant values are in bold.

	Hg	TOC	Fe	Mn	% Silt–clay	% S
BCCF10-01						
Hg	1.00					
COT	–0.21	1.00				
Fe	<b>–0.45</b>	0.05	1.00			
Mn	–0.31	0.20	<b>0.49</b>	1.00		
% Silt–clay	0.00	0.27	0.01	–0.08	1.00	
%S	<b>–0.42</b>	0.27	0.24	0.08	0.31	1.00
BCCF10-04						
Hg	1.00					
COT	–0.08	1.00				
Fe	–0.08	<b>0.67</b>	1.00			
Mn	0.13	0.04	<b>0.38</b>	1.00		
% Silt–clay	0.08	0.00	0.12	0.04	1.00	
%S	–0.04	<b>0.66</b>	0.45	–0.10	0.29	1.00
BCCF10-09						
Hg	1.00					
COT	–0.27	1.00				
Fe	–0.29	<b>0.47</b>	1.00			
Mn	<b>0.77</b>	0.04	–0.10	1.00		
% Silt–clay	<b>–0.59</b>	<b>0.44</b>	<b>0.43</b>	<b>–0.43</b>	1.00	
%S	<b>–0.50</b>	0.20	<b>0.38</b>	<b>–0.41</b>	0.45	1.00
BCCF10-15						
Hg	1.00					
COT	–0.06	1.00				
Fe	–0.16	–0.21	1.00			
Mn	–0.20	<b>–0.64</b>	<b>0.70</b>	1.00		
% Silt–clay	–0.40	–0.27	0.13	0.23	1.00	
%S	0.45	<b>0.50</b>	–0.25	<b>–0.69</b>	–0.30	1.00

Hg imported was used in the chlor-alkali industries, which is responsible for more than 80% of the total mercury imported by Brazil until the 80s (Lacerda, 1997).

Another source of mercury in the 80s could be attributed to the Paraíba do Sul River, considered the main point source of this metal to the continental shelf northeast of Rio de Janeiro, as this river was widely impacted by sugar cane plantation until 1980 (Lacerda et al., 1993). However, Lacerda et al. (1993) demonstrated a low influence of the Paraíba do Sul river plume beyond the 10 m isobaths, and a decrease in the concentrations of Hg in surface sediments have been noted with increasing distance to the coastline. Furthermore, Molisani et al. (1999) found a low influence of the Paraíba do Sul River in the transport of metals to the Atlantic Ocean.

Upwelling zones have been related with an Hg supply to ocean's surface waters (Mason and Fitzgerald, 1991; Cossa et al., 2004; Soerensen et al., 2010). Furthermore, upwelling regions have been of the great importance to Hg biogeochemical cycle due to the high productivity and large organic matter deposition in these areas (Rolfhus and Fitzgerald, 1995; Silva et al., 2011), which may explain the relatively high Hg flux, as compared to other regions of the globe and suggest that lateral transport is an important source of Hg to the Cabo Frio region.

The cumulative inventory quantifies the total amount of Hg loaded to the sediments. Through this calculation, a quantified and evaluated influence of anthropogenic Hg in the region may be noted. The inventory was determined by the following equation:  $Hg\ Inv\ (ng\ cm^{-2}) = \sum [(Hg_i - Hg_{background}) \cdot d \cdot \rho]$  (Covelli et al., 2006) where  $Hg_i$  is the concentration of metal measured;  $Hg_{background}$  is the concentration of the background Hg established for the region,  $d$  is the layer thickness and  $\rho$  is the sediment layer density.

The Hg background concentration was determined by averaging the sedimentary layers below those deposited during the past 130 years, according to Hare et al. (2010). This time period was extrapolated from the dating methods referenced in this work,

**Table 4**

Mercury accumulation rate, peaks, average and inventory.

Area	Hg total accumulation rate ( $ng\ cm^{-2}\ y^{-1}$ )			Hg inventory ( $ng\ cm^{-2}$ ) (100 y)	Hg excess ( $ng\ cm^{-2}$ ) (100 y)	Hg excess ( $ng\ cm^{-2}$ ) (30 y)
	Average	Peak	Years			
BCCF10-01	1.55	3.72	1905	2041	655.6	148.8
BCCF10-04	2.36	5.82	2002	2681	820	331
BCCF10-09	8.34	20.0	1982	13036	9035	2159
BCCF10-15	6.00	10.7	1995	–	–	1845
						502

based on this time period, Hg background concentration were established to be  $8\ ng\ g^{-1}$ . As a result, large Hg accumulation was noted over the past 100 years on the Cabo Frio continental shelf, with emphasis on the BCCF10-09 area, which showed a value of inventory approximately 6 times higher than the BCCF10-01 area (Table 4). The excess Hg corresponded to approximately 70% of the total inventory for the past 100 years in the BCCF10-09 area, while the cores BCCF10-01 and BCCF10-04 the values were near to 30% (Table 4). Guanabara Bay, Southwest of the Cabo Frio, has a long history of Hg contamination. Indeed values found in the sediments of this Bay have shown to be extremely high during the previous 60 years ( $1.05\text{--}777\ mg\ m^{-2}$ ) (Machado et al., 2008), ( $26\text{--}91\ mg\ m^{-2}$ ) (Covelli et al., 2012) which may be laterally transported and contribute to the high Hg inventory found in Cabo Frio.

When comparing the excess Hg in Cabo Frio with values located in sub-Arctic ( $16\ a\ 173\ ng\ cm^{-2}$ ) (Hare et al., 2010) and Greenland ( $21\ a\ 57\ ng\ cm^{-2}$ ) (Bindler et al., 2001) to the same time interval, the values shown in this work are at least one order of magnitude higher. The Northern Hemisphere studies suggest that atmospheric deposition is the main input of Hg to continental shelves. Here we show that Hg depositional fluxes on the Cabo Frio continental shelf are directly related to the relatively high silt–clay and organic matter burial in specific depot areas. Therefore, the temporal Hg enrichment on the continental shelf is likely caused by point source pollution, lateral transport and particulate matter scavenging in this active upwelling region.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.marpolbul.2013.07.049>.

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