Bull. Environ. Contam. Toxicol. (2004) 72:178–185

DOI: 10.1007/s00128-003-0257-0

Environmental Contamination and Toxicology

Mercury Distribution in Continental Shelf Sediments from Two Offshore Oil Fields in Southeastern Brazil

L. D. Lacerda,[1,2] C. E. Rezende,[3] Á. R. C. Ovalle,[3] C. E. V. Carvalho[3]

[1] Instituto de Ciências do Mar (LABOMAR), Universidade Federal do Ceará, Av. Abolição 3207, Fortaleza, 60165-081, CE, Brazil
[2] Departamento de Geoquímica, Universidade Federal Fluminense, Niterói, RJ, Brazil (*on leave*)
[3] Laboratório de Ciências Ambientais (CBB), Universidade Estadual do Norte Fluminense, Av. Alberto Lamego, 2000, Campos dos Goytacazes, 28015-620, RJ, Brazil

Received: 3 December 2002/Accepted: 8 September 2003

Most anthropogenic environmental impacts on marine areas are limited to protected coastal sites such as bays and estuaries, or semi-enclosed seas (Irion and Muller 1990). It is believed that open continental shelves are hardly affected by land-based pollutants sources. Exceptionally, offshore oil exploration is considered a potential source of pollutants to continental shelf environments both when drilling for prospecting (Rezende et al. 2002) and during oil production and transport (Kennicutt 1995). Whereas hydrocarbons may be released by offshore oil exploration and affect water masses for a varying time depending on their degradability, heavy metals and particularly Hg, that are ubiquitous components of oil industry effluents, are non-degradable and may accumulate in abiotic and biotic compartments reaching potentially toxic concentrations particularly in nearby bottom sediments (Rezende et al. 2002). The large Hg accumulating capacity of fine bottom sediments of continental shelves (Muller et al. 1999) and the low mobility of the benthic communities, maximize exposure and make possible deleterious effects upon the biota potentially affecting economically important open ocean fisheries through food chain transfer and biomagnification (Chapman et al. 1991). Although effects upon shelf biota are difficult to detect and monitor, the importance of shelf resources and the possibility of fisheries contamination by long-lasting contaminants such as Hg call for detailed studies in areas affected by oil exploration (Lacerda et al. 2000; Kennicutt 1995).

The Bacia de Campos oil field (Fig. 1) is the largest Brazilian oil prospecting and production area, with average output of 1 million BPD of oils and 12,450 $m^3.d^{-1}$ of gas, about 60% of the total Brazilian production. Estimated reserves reach 96% of the country's total and operations range from a depth of 100 to 1,200 m. In 1997 the PETROBRAS Company, which runs the field, started an environmental monitoring program to investigate potential contamination of the local environment, in particular by trace metals (PETROBRAS 2001). As an output of that program this study shows the distribution and geochemical association of Hg in bottom sediments surrounding two of the most important oil exploration platforms in the area, located in the outer shelf off the Paraíba do Sul River mouth (Fig. 1), to test the potential effects of their operation on the distribution and

Correspondence to: L. D. Lacerda

concentration of Hg. Inner shelf sediments were also sampled to serve as continental-influenced end-member of Hg concentrations.

MATERIALS AND METHODS

The Campos continental shelf and offshore oil fields are located in Rio de Janeiro State, SE Brazil (Fig. 1) from latitudes 21° S and 23° S. It is dominated by the 2,000 km^2 Paraíba do Sul Coastal Plain. Climate is humid sub-tropical with annual rainfall of about 1,200 mm, distributed in a summer rainy season between November and February and a dry winter in June-August (Ekau and Knoppers 1999).

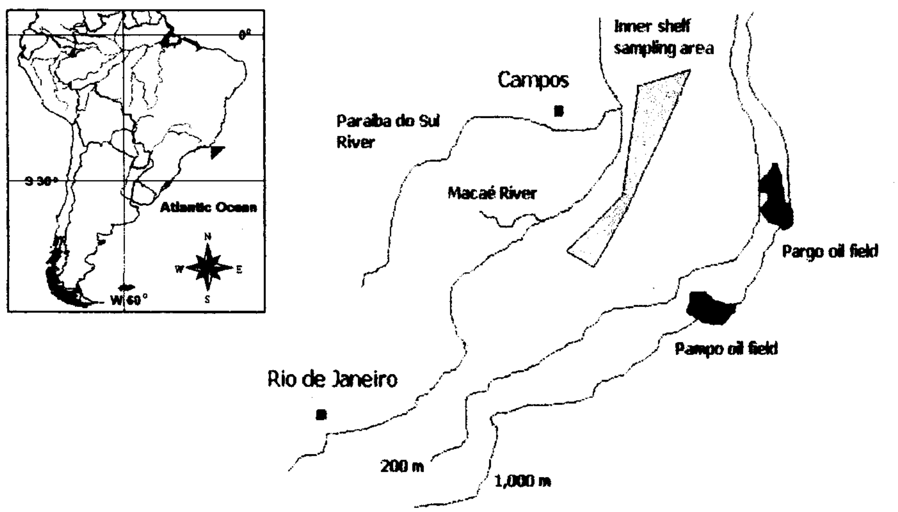

Figure 1. Physiographic features of the Campos continental shelf and location of the studied areas at the inner shelf and surrounding the Pargo and Pampo oil exploration platforms.

Freshwater discharge is mostly from the Paraíba do Sul River (> 80% of the total), followed by the Itaboapoana and Macaé Rivers and varies from 200 to 4,380 $m^3.s^{-1}$ during the dry and rainy season respectively. Long-term annual average is about 2,000 $m^3.s^{-1}$ (Salomão et al. 2001).

The continental shelf width ranges from 45 to 90 km with a breakdown at about 70 to 100 m depth. Bottom sediments are mostly of modern terrigenous origin, with spots of relict sediments from past sea level change and an enrichment of carbonates at the outer shelf. Mineralogy is dominated (>80%) by kaolinite (Massé et al. 1996). Sediment traps deployed at the Paraíba do Sul River mouth showed the terrigenous flux to drift southward more or less parallel to the shore, due to the prevalence of Northeastern winds. River plumes edge along the coast being diluted by tropical surface waters within a few kilometers from the river mouths. However, terrigenous fine materials are transported to the shelf slope (Jennerjahn and Ittekkot 1997; Ekau and Knoppers 1999) and may eventually reach the oil exploration area. The knowing of the extent of the influence of river plumes is of key importance to evaluate the potential effect of offshore oil activities on the Hg distribution in shelf sediments.

Our results are based on samples collected in concentric circles located 250 m, 500 m, 1,000 and 3,000 m from each platform: Pampo (Lat. 22°48'32''S; Long. 40°46'41''W) and Pargo (Lat. 22°15'26''; Long. 40°19'51''W) both located south of the Paraíba do Sul River mouth. Inner shelf sediments were collected within the 95 to 110 m isobaths along the Campos coast (Fig. 1). Sampling campaigns occurred during the winter and summer of 1998 and 1999. Four samples of surface sediments (0-3 cm of depth) were collected in each station during each campaign using a box corer. In the laboratory samples were sieved (< 1.0 mm) to avoid dilution due to larger sand grains and debris and dried (40°C for 72 h). Total Hg content was determined by Cold Vapor Atomic Absorption Spectrophotometry after an acid digestion of 4 g of dry sediment with a 50% $HCl:HNO_3$; 1:1 solution. Details on the chemical procedures used can be found in Marins et al. (1998). Simultaneous analysis of reference standard material (NIST 1646a, Estuarine Sediment) using the same procedure, reached a good agreement between certified and measured concentrations (60 ± 2.0 vs 58 ± 3.2 $ng.g^{-1}$ dry weight, respectively).

A non-parametric two-way analysis of variance showed no difference between winter and summer samplings and a Kruskal-Wallis non-parametric test showed no difference between different distances from the platforms. Therefore, samples from the two cruises were pooled to study differences in Hg concentrations between platforms and the inner shelf sediments.

RESULTS AND DISCUSSION

The interplay between terrigenous and carbonate sedimentation controls sediment distribution on the shelf area studied, the higher the fluvial input the lower the carbonate sediment (Ekau and Knoppers 1999). Modern terrigenous contribution, represented by higher silt and clay content and lower carbonate, is more clearly observed in the inner shelf, where inputs from rivers are dominant, particularly the Paraíba do Sul River, which sediments reach the external continental platform and mean sediment flux to the sea reaches 1.0 to 2.0×10^6 $t.yr^{-1}$ (Carvalho et al. 2002).

Inner shelf sediments presented variable concentrations of organic carbon and silt and clay. They were richer in organic carbon and silt and clay content than the Pargo platform sediments but lower than Pampo platform sediments (Table 1). The carbonate concentrations best discriminate between inner shelf sediments and those from the outer shelf. Much lower concentrations (<3.0%) were found in inner shelf sediments compared to those around the oil platforms, where average carbonate contents varied from 20.1 to 64.3 % (Table 1). The high concentrations of biogenic carbonates (>50%) also resulted in higher concentrations of organic matter (up to 2.72 %), one order of magnitude higher than in inner shelf samples. Similar results were reported for the Northeastern Brazilian continental shelf (Muller et al. 1999).

The distribution of major geochemical variables therefore, suggests that at the location of the oil platforms, the terrestrial material signature is diluted, but still observed in both platform areas. Sediments around the Pampo platform probably receive more influence from continental derived materials, since this area is located directly to the south of the Paraíba do Sul River mouth, which sediment plume runs in that direction along the coastline (Lacerda et al. 1993). Pargo sediments, on the other hand, seem more influenced by alloctonous materials represented by carbonates. The carbonates sedimentation facies there suggest significant changes in oceanographic circulation showing encrusting red algae with the presence of mollusks, bryozoans and foraminifers. Also, paleo-oceanographic inferences based on proportion of plancktonic to benthic foraminifers showed good preservation conditions (PETROBRAS 2001). This supports the hypothesis of less continental influence on Pampo sediments relative to Pargo and inner shelf samples.

Table 1. Mean, standard deviation and range of concentrations of major sedimentological characteristics and Hg concentrations of shelf sediments from the Campos offshore oil fields. (dry weight basis; n=24).

Site	C-org (%)	$CaCO_3$ (%)	Silt/Clay (%)	Al ($mg.g^{-1}$)	Fe ($mg.g^{-1}$)	Hg ($ng.g^{-1}$)
Inner	0.86 ± 0.90	0.77 ± 0.95	36 ± 38.2	21.1 ± 5.9	9.86 ± 3.9	47.3 ± 19.2
shelf	<0.05-2.45	<0.01-2.66	<0.2-96.9	11.2-31.4	6.1-16.4	13 - 80.0
Pargo	0.19 ± 0.06	25.8 ± 5.7	11.1 ± 6.1	6.79 ± 3.6	6.92 ± 2.9	38.9 ± 12.3
Field	0.09-0.29	20.1-39.6	1.7-31.8	4.32-11.1	4.43-9.2	11.5-61.0
Pampo	1.43 ± 0.43	51.2 ± 11.7	98.9 ± 1.6	6.92 ± 2.9	5.81 ± 2.3	36.4 ± 13.1
Field	0.92-2.72	37.4-64.3	94.5-100	4.43-9.18	4.4-8.4	25.5-61.9

The three sampling areas showed significant statistical differences in the concentrations of terrigenous elements (Al and Fe) (Table 1). Inner shelf sediments presented the highest concentrations whereas the areas under the influence of the two platforms showed similar but lower concentrations for both metals. Aluminum has been successfully used as tracer of terrestrial-born sediments in different areas of the Brazilian continental shelf (Carvalho et al. 1993) whereas Fe has been used by Arz et al. (1999) to study changes in the intensity of the terrigenous sediment flux to the Northeastern Brazil continental shelf. Aluminum is mostly derived from abundant feldspars ($K[AlSi_3O_8]$) from the Pre-Cambrian granites typical of the coastal basin geology. The dominance of kaolinite in these sediments supports this hypothesis (Muller et al 1999). Iron is transported to the sea as hydrated oxides associated with clays from the weathering of rocks. In shelf sediments Al and Fe are generally associated with the fine fraction ($62 < \mu$) of sediments (Muller et al. 1999; PETROBRAS 2001).

Mercury concentrations were variable within and between sampling sites with standard deviation being about 40% of the mean. This makes difficult the testing of significant statistical differences between sampling sites. Inner shelf sediments presented Hg concentrations varying from 13 to 80 $ng.g^{-1}$ and were significantly higher, but with only $P<0.1$, than the concentrations found in outer shelf sediments close to the platforms, which varied from 11.5 to 61.9 $ng.g^{-1}$. These, on the other hand, were similar between the two platforms. Inner shelf sediment Hg concentrations clearly reflect the inputs from terrigenous sources. Sediments from the Paraíba do Sul River, for example, present Hg contents of up to 550 $ng.g^{-1}$ in along its lower course due to contamination by effluents from industrial, agriculture and mining activities (Pfeiffer et al. 1989). No data on Hg concentrations in sediments of the lower basins of other rivers in the region is available, but concentrations ranging from 50 to 250 $ng.g^{-1}$ have been reported for the upper reaches of the basin's fluvial systems (Lima 1990). The Paraíba do Sul River plume, which spreads south of the river mouth, also presents higher Hg concentrations ranging from 50 to 145 $ng.g^{-1}$ (Lacerda et al. 1993). Our results confirm the previously suggested influence of fluvial materials upon the inner shelf (Carvalho et al. 1993). The maximum values measured in stations from the outer shelf are higher than background concentrations for southeastern Brazil coastal sediments, which typically range form 10 to 50 $ng.g^{-1}$ (Lacerda et al. 1993; Marins et al. 1998). Although the highest concentrations were found in less than 20% of the samples they showed no trend regarding the distance from the platforms, but were generally found at stations enriched in silt and clay, Al and Fe, suggesting a residual influence of continental materials.

The Paraíba do Sul River is a significant exporter of heavy metals and suspended matter to inner shelf sediments. A recent estimate of heavy metals and suspended matter (SPM) fluxes from this river to the ocean based on monthly distribution and loads estimates, gives annual inputs of the order of thousand tons: (SPM = 0.8 to 2.1 x 10^9 kg; Fe = 0.7 to 1.5 x 10^8 kg; Mn = 1.4 to 3.2 x 10^6 kg; Zn = 0.2 to 0.5 x 10^6 kg; and Cu = 0.09 to 0.14 x 10^6 kg) (Salomão et al. 2001; Carvalho et al. 2002). Although no data on Hg flux is available, our results strongly suggest that the continental contribution can reach the outer shelf rather than being a signature of the offshore oil exploration. Different authors (Carvalho et al. 1993; Tiltenolt 1996; Muller et al. 1999) have reported the significance of continental inputs to trace metals concentration and distribution in sediments from other sectors of the Brazilian continental shelf, others authors (PETROBRAS 2001; Rezende et al. 2002) found no effect of oil drilling and production operations on the trace metals distribution in continental shelf sediments, suggesting that any anomaly in heavy metal concentrations is of continental origin.

A matrix of correlation coefficients between pair of elements and between elements and sedimentological parameters is presented in table 2, for inner and outer shelf sediments. The correlation coefficients confirm the hypothesis of a generalized influence of terrestrial materials, delivered by the Paraíba do Sul River, as the major source of Al, Fe and Hg to inner shelf sediments. All metals in inner shelf sediments are significantly and positively correlated with organic carbon and the silt and clay fraction of sediments. Also they present negative correlation with carbonate concentrations, a typical indicator of marine, autochthonous sediments. Similar correlations have been found by other authors in inner shelf sediments close to significant river inputs regarding other trace metals of environmental significance (Carvalho et al. 1993; 2002; Muller et al. 1999).

At the outer platform, Fe and Al still correlates significantly but not with Hg, suggesting a larger dilution of Hg relative to those more conservative elements. Hg distribution in these sediments seems to be independent of all variables measured and is probably a result of the interaction between the continental Hg flux and the environmental conditions of coastal areas which generate a diversity of Hg soluble forms and their complex behavior in coastal areas, particularly its interactions with dissolved organic matter and suspended solids, as seem from the significant correlations (Table 2) with these parameters in inner shelf areas (Lacerda and Gonçalves 2001).

Table 2. Correlation matrix between Hg concentrations and selected geochemical parameters in bottom sediments from the SE Brazilian continental shelf under the influence of offshore oil exploration.

Pargo St.	Hg	C-Org.	$CaCO_3$	Silt-clay	Fe	Al
Hg	1.000					
C-Org.	0.240	1.000				
$CaCO_3$	-0.154	-0.215	1.000			
Silt-clay	0.200	-0.130	0.090	1.000		
Fe	0.453	0.144	-0.117	0.119	1.000	
Al	0.086	-0.094	-0.029	0.440	0.608*	1.000

Pampo St.	Hg	C-Org.	$CaCO_3$	Silt-clay	Fe	Al
Hg	1.000					
C-Org.	0.294	1.000				
$CaCO_3$	-0.146	-0.281	1.000			
Silt-clay	0.357	-0.115	-0.324	1.000		
Fe	-0.012	0.029	-0.438	0.432	1.000	
Al	-0.110	0.185	-0.681*	0.385	0.680*	1.000

Inner Shelf	Hg	C-Org.	$CaCO_3$	Silt-clay	Fe	Al
Hg	1.000					
C-Org.	0.795*	1.000				
$CaCO_3$	-0.366	-0.478	1.000			
Silt-clay	0.786**	0.890**	-0.608*	1.000		
Fe	0.804**	0.913**	-0.457*	0.895**	1.000	
Al	0.801**	0.894**	-0525*	0.918**	0.935**	1.000

(* $P<0.05$; ** $P<0.01$; $n = 20$)

The results presented in this study suggest that the terrigenous influence on continental platform sediments in southeastern Brazil can reach the outer shelf areas, where most of the offshore oil fields are located. The strong signature of terrestrial materials at the outer shelf and the lack of association between Hg and the other measured parameters makes difficult to assess any effects of the oil producing activities on Hg concentrations in bottom sediments, thus making the monitoring of its potential impacts very difficult, being necessary a larger number of samples and sampling frequency in order to separate the continental signature.

Acknowledgments. This study was supported by the PETROBRAS Oil Company, Brazil, as a part of its monitoring efforts on the Campos Offshore Oil Filed (PETROBRAS-BIORIO Contract 960020), and a PRONEX Program Grant CNPq 466.090/2001-3. Authors, LDL, ARC and CER received fellowships from CNPq. We thank the Arizoli AR Gobo and Ayres G.A. for laboratory and field support.

REFERENCES

Arz HW, Patzold G, Wefer G (1999) Climatic changes during the last glaciation recorded in sediment cores from the northeastern Brazilian Continental Margin. Geo-Marine Lett 19:209-218

Carvalho CEV, Lacerda LD, Rezende CE, Ovalle ARC, Abrão JJ (1993) The fate of heavy metals in sediments of the northeastern and southeastern Brazilian continental shelf. In: Allan RJ, Nriagu JO (ed) Proc Inter Conf Heavy Metals in the Environment, Toronto, CEP Consultants, Edinburgh, 1:153-156

Carvalho CEV, Salomão MSMB, Molisani, MM, Rezende CE, Lacerda LD (2002) Contribution of a medium-sized tropical river to the particulate heavy-metal load for the South Atlantic Ocean. Sci Tot Environ 284:85-93

Chapman PM, Power EA, Dexter RN, Andersen HB (1991) Evaluation of effects associated with an oil platform, using the sediment quality triad. Environ Toxicol Chem 10:407-424

Ekau W, Knoppers BA (1999) An introduction to the pelagic system of the East and Northeast Brazilian shelf. Arch Fish Mar Res 47:1-17

Irion G, Muller G (1990) Lateral distribution and sources of sediment-associated heavy metals in the North Sea. In: Ittekkot V, Kempe S, Michaelis W, Spitzy A. (ed) Facets of Modern Biogeochemistry, Springer Verlag, Berlin, p. 175-201

Jennerjahn TC, Ittekkot V (1997) Organic matter in sediments in the mangrove areas and adjacent continental margins of Brazil: I. Amino acid and hexosamines. Oceanologica Acta 20:359-369

Kennicutt MC (1995) Gulf of Mexico offshore operations monitoring experiment, Phase I: Sub lethal responses to contaminant exposure. Final Report. OCS Study MMS95-0045 US Department of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, New Orleans, Louisiana, 709p

Lacerda LD, Carvalho CEV, Rezende CE, Pfeiffer WC (1993) Mercury in sediments from the Paraiba do Sul River continental shelf, SE Brazil. Mar Pollut Bull 26: 220-222

Lacerda LD, Paraquetti HHM, Marins RV, Rezende CE, Zalmon IR, Gomes MP, Farias V (2000) Mercury content in shark species from the Southeastern Brazilian coast. Rev Brasil Biol 60: 1-6

Lacerda LD, Gonçalves GO (2001) Mercury distribution and speciation in waters of the coastal lagoons of Rio de Janeiro, SE Brazil. Mar Chem 76: 47-58

Lima ECR (1990) Riscos e conseqüências do uso do mercúrio: a situação do Rio de Janeiro. In: Hacon S, Lacerda LD, Pfeiffer WC, Carvalho D (eds). Riscos e Conseqüências do Uso do Mercúrio. FINEP/UFRJ, Rio de Janeiro, p: 268-280

Marins RV, Lacerda LD, Paraquetti HHM, Paiva EC, Villas Boas RC (1998) Geochemistry of mercury in sediments of a sub-tropical coastal lagoon, Sepetiba bay, Southeastern Brazil. Bull Environ Contam Toxicol 61: 57-64

Massé L, Faugéres JC, Pujol C, Pujos A, Labeyrie LD, Bernat M (1996) Sediment flux distribution in the Southern Brazil Basin during late Quaternary: The role of deep-sea currents. Sedimentology 43:115-132

Muller G, Irion -G, Morais JO, Tintelnot M (1999) Heavy metal concentrations in fine grained sediments in the lower course of Brazilian rivers between the state of Piauí and Espírito Santo. In: Abrão JJ (ed) Proc 3rd Inter Symp Environmental Geochemistry in Tropical Countries. Univ Fed Fluminense, Niterói, p, 1-4

PETROBRAS (2001) Monitoramento ambiental da atividade de produção de petróleo na bacia de Campos. Etapa de Pré-Monitoramento. Final Report, PETROBRAS Petróleo Brasileiro SA, Rio de Janeiro, 222p

Pfeiffer WC, Souza CMM, Malm O, Bastos WR, Torres JP (1989) Mercury pollution from gold mining areas of the State of Rio de Janeiro, Brazil. Proc 7th Inter Conf Heavy Metals in the Environment 1:222-225

Rezende, CE, Lacerda, LD, Ovalle, ARC, Souza, CMM, Gobo, AAR, Santos, DO (2002). The effect of an oil drilling operation on the trace metal concentrations in offshore bottom sediments of the Campos Basin oil field, SE Brazil. Mar Pollut Bull 44: 680-684

Salomão MSMB, Molisani MM, Ovalle ARC, Rezende CE, Lacerda LD, Carvalho CEV (2001) Particulate heavy metal transport in the lower Paraíba do Sul River Basin, southeastern Brazil. Hydrolog Proc 15: 587-593