

Metals in water, sediments, and biota of an offshore oil exploration area in the Potiguar Basin, Northeastern Brazil

L. D. Lacerda · R. C. Campos · R. E. Santelli

Received: 3 February 2012 / Accepted: 11 September 2012 / Published online: 27 September 2012
© Springer Science+Business Media B.V. 2012

Abstract Metal concentrations were evaluated in water, bottom sediments, and biota in four field campaigns from 2002 to 2004 in the Potiguar Basin, northeastern Brazil, where offshore oil exploration occurs. Analyses were performed by inductively coupled plasma mass spectrometry and inductively coupled plasma optical emission spectrometry. Total metal concentrations in water (dissolved+particulate) and sediments were in the range expected for coastal and oceanic areas. Abnormally high concentrations in waters were only found for Ba ($80 \mu\text{g l}^{-1}$) and Mn ($12 \mu\text{g l}^{-1}$) at the releasing point of one of the outfalls, and for the other metals, concentrations in water were found in stations closer to shore, suggesting continental inputs. In bottom sediments, only

Fe and Mn showed abnormal concentrations closer to the effluent releasing point. Metal spatial distribution in shelf sediments showed the influence of the silt–clay fraction distribution, with deeper stations at the edge of the continental shelf, which are much richer in silt–clay fraction showing higher concentrations than shallower sediments typically dominated by carbonates. Metal concentrations in estuarine (mollusks and crustaceans) and marine (fish) organisms showed highest concentrations in oysters (*Crassostrea rhizophorae*). Fish tissues metal concentrations were similar between the continental shelf influenced by the oil exploration area and a control site. The results were within the range of concentrations reported for pristine environments without metals contamination. The global results suggest small, if any, alteration in metal concentrations due to the oil exploration activity in the Potiguar Basin. For monitoring purposes, the continental inputs and the distribution of the clay–silt fraction need to be taken into consideration for interpreting environmental monitoring results.

L. D. Lacerda (✉)
Instituto de Ciências do Mar, Universidade
Federal do Ceará,
Fortaleza, CE 60165-081, Brazil
e-mail: ldrude@pq.cnpq.br

R. C. Campos
Departamento de Química, Pontifícia Universidade
Católica do Rio de Janeiro,
Rio de Janeiro, Rio de Janeiro 22450-051, Brazil
e-mail: recampos@puc-rio.br

R. E. Santelli
Departamento de Geoquímica,
Universidade Federal Fluminense,
Niterói, Rio de Janeiro 24020-007, Brazil
e-mail: santelli@geoq.uff.br

Keywords Metals · Water · Sediments · Biota ·
Offshore oil exploration · Continental platform

Introduction

Contamination of the marine environment originates from diverse anthropogenic sources. Terrestrial sources contribute with 70 to 80 % of contaminant emissions to

coastal areas, whereas from 20 to 30 % of emissions originate from activities located in situ, mostly associated with maritime transport, exploration of mineral resources, prospecting and exploration of offshore oil, and natural gas and discharges from submarine outfalls (Crossland et al. 2005).

Among the contaminants present in these effluents, pathogenic microorganisms, organic matter, nutrients, organic micropollutants, hydrocarbons, and metals are the most significant (Marcovecchio 2000). These substances reach coastal waters through rivers and atmospheric deposition. Nondegradable substances, such as metals, are of particular environmental concern, due their inherent toxicity and possibility of geoaccumulation to relative high concentrations in marine bottom sediments, bioaccumulation and transfer through food chains (Marins et al. 1998; Marcovecchio 2000).

Prospecting and exploration of offshore oil and natural gas have recently achieved environmental significance due to increasing known reserves throughout the world and the rising of oil prices, which allowed their economic exploitation under offshore conditions. These activities may be important sources of organic contaminants to the oceans and their visual and shocking impacts when accidents occur resulted in increasing public awareness of their environmental significance. However, offshore oil and gas prospecting and production also emit other contaminants to the marine environment, in particular metals, which are still poorly documented for most exploitation areas worldwide. Metals are ubiquitous components of many exploration platform effluents, perforation fluids, and produced waters. They are also present in effluents from water treatment plants located onshore (Neff 2002; Rezende et al. 2002; Trefry et al. 2003; Pozebon et al. 2005), refineries (Ramos et al. 2012), fly ash from coal burning power stations (Haynes et al. 1997; Haynes and Johnson 2000), and coastal landfills (Hübner et al. 2010).

On the other hand, metals are also found in varying concentrations in natural substrates (water, sediments, and biota), depending on geological, oceanographic, and ecological conditions of a given area, making it extremely difficult to differentiate between eventual contributions from anthropogenic sources from the natural background (Freire et al. 2004; Rezende et al. 2004).

Produced water is the major effluent of offshore oil and gas production. Globally, it accounts for daily emissions of over 17 million cubic meters. About 40 % only ($7 \text{ million m}^3 \text{ day}^{-1}$) is released to the sea prior to or after

treatment for reduction of particulate matter and hydrocarbons (OGP 2005). The ratio between oil and produced water in mature fields may reach 1:10 and it increases with aging. Thus, an overall increase in produced water release with time is expected (OGP 2005). Chemical composition of produced water is complex and depends on the oil or gas field and is in equilibrium with the reservoir characteristics and geological formation. Apart from major constituents such as chlorides, sulfate, iron, boron, and barium, some metals of environmental significance, in particular, Cu, Zn, Mn, Ni, Fe, and V, may also present relatively high concentrations (Kennicutt et al. 1996a; Kennicutt et al. 1996b; Utvik 1999; Gabardo et al. 2005). Therefore, due to the naturally very low concentrations of metals found in the pristine marine environment and the increasing release of produced waters from oil and natural gas offshore exploitation, assessment, and monitoring of their concentrations in areas under the influence of offshore operations are mandatory steps in the environmental regulation of this activity. Unfortunately, many inherent aspects of metals distribution in offshore environments make difficult the recognition of impacts from offshore oil and gas exploration on metals concentrations.

Metals are poorly soluble in seawater, and the large dilution factors result in extremely low concentrations even close to sources. Such low levels together with the interferences caused by the saline matrix make the analytical detection a challenging task. Therefore, concentrations of metals in the Brazilian continental shelf waters are very poorly known, being restricted to protected areas close to contamination sources located onshore. Sediments, on the other hand, may integrate metals reaching the sedimentary environment of the continental shelf making easier their analysis and this resulted in a few comprehensive studies on their distribution in Brazilian continental shelf sediments (Freire et al. 2004; Rezende et al. 2004; Lacerda and Marins 2006). In the oil exploration area of the Campos Basin in southeastern (SE) Brazil, for example, Rezende et al. (2002) showed no effect on metal concentrations in sediments collected as close as 500 m from producing oil platforms. During drilling, a small increase in the concentrations of Zn, Ni, and Al was reported close to the drilling operation, but it could not be detected after 6 months from closing operations.

Apart from the generally low concentrations in effluents from the offshore oil and gas exploration, the natural variability of metals concentrations in continental

shelf sediments may be very large due to the strong influence of continental inputs of relatively metal-rich materials. For example, at the same Campos Basin exploration area, the input of Hg from rivers may reach the outer continental shelf (Lacerda et al. 1993), making extremely difficult the differentiation between natural from locally generated anthropogenic inputs of Hg. Also, natural inputs from continental sources also present a strong seasonal component (Molisani et al. 1999; Salomão et al. 2001; Carvalho et al. 2002), which may result in varying distribution of continental derived metals in shelf sediments.

Distribution of metals in the biota under the influence of oil and natural gas offshore exploitation are poorly known and restricted to offshore areas in the Gulf of Mexico (Trefry et al. 1995), Norway (OGP 2005), and Thailand (Windom and Crammer 1998). No evidence so far, suggested any influence of metal release from the activity on their concentration in the marine biota. Along the Brazilian coast, metals concentrations in marine biota close to exploitation areas are restricted to results obtained in samples of adherent organisms collected on the structure of offshore exploitation platforms. These few available results, however, also failed to discriminate between metals originated in effluents from those originated in the metallic structure itself and are of small monitoring significance (Paranhos and Ximenez 2005).

The Potiguar Basin is an oil and natural gas production area located in northeastern (NE) Brazil. The production area is 40 % onshore, constituted of about 3,000 small production wells and 60 % offshore, represented by 34 production platforms. Produced water from both areas is treated onshore and the effluents released by two submarine outfalls in the continental shelf. Effluents flux from the outfalls average $160,000 \text{ m}^3 \text{ day}^{-1}$ and the production water treatment plant are in full operation since 2001. Some produced water ($80,000 \text{ m}^3 \text{ day}^{-1}$) has been directly released at sea between 1998 and 2001, but re-injection procedures and the completion of the Guamaré Treatment Plant, presently avoid this practice (Gabardo et al. 2005; PETROBRAS [Petróleo Brasileiro S.A.] 2006).

This paper presents a synthesis of the results from a 3-year monitoring program on metal distribution in water, bottom sediments, and biota of the Potiguar Basin, in order to test if the presence of operational platform and/or the release of effluents from the production water treatment plant result in alterations of

metal concentrations in these environmental compartments, after nearly 5 years of operation. The monitoring program included the continental shelf proper, where most exploration platforms are located and the shallow coastal areas, which are mostly under the influence of effluents discharged by the submarine outfalls from the produce water treatment plant located onshore.

Study area

The coastal zone adjacent to the major oil exploitation basins in NE Brazil is characterized by a relatively narrow coastal plain (50 to 100 km) composed by Tertiary siliclastic gross sediments (Barreiras Formation) limited inland by the granite outcrops of the Pre-Cambrian Brazilian shield. This geology is the major source of continental materials to the ocean. Total continental drainage basin of the region is about $200,000 \text{ km}^2$ and fluvial inputs to the ocean reaches about $200 \text{ m}^3 \text{ s}^{-1}$. Climate varies from humid ($1,000$ to $1,200 \text{ mm year}^{-1}$) at mountain ranges and coastal valleys, to semi-arid (500 a 700-mm year^{-1}) in the lowlands. Coastal soils are podsoles and oxisols within extensive dune fields and sandy beaches. Mangroves dominate estuaries and coastal lagoons. The continental shelf shows low declivity down to 70 m deep (1:670 to 1:1,000) and width ranging from 40 km at the east extreme to 100 km at the west sector (Martins and Coutinho 1981; Arz et al. 1999).

Three parallel sedimentary zones are recognized for this sector of the Brazilian continental shelf. From the beach limit to about 20 m deep, a first zone dominated by quartz sands and siliclastic sediments of continental origin is present. This is followed by a zone dominated by bioclastic sediments, in particular carbonates from calcareous algae, mostly of the *Lithothamnium* spp. (Rodophyta) and *Halimeda* spp. (Clorophyta), extending to 70 m of depth. At the edge of the continental shelf, terrigenous siliclastic sediments dominate again (Summerhayes et al. 1975; Nascimento et al. 2010). Continental shelf sedimentation is, therefore, defined by the relative importance of these major sources where the higher the relative importance of calcareous (marine; organogenic) sediments the lower the relative importance of siliclastic (terrigenous) sediments (Milliman and Summerhayes 1975; Knoppers et al. 1999).

Materials and methods

Sample collection

All water and sediment samples were collected in four campaigns at roughly 8-month intervals from the ship *N/RB Astro Garoupa* from the Brazilian oil company, PETROBRAS S.A. Location of sample stations were the same for water and sediments and DGPS positioning reduced vessel shift between campaigns to less than 100 m. Marine biota samples were collected by hand along estuaries, whereas marine fish were sampled from the ship *N/Oc. Prof. Martins Filho*, from the Federal University of Ceará. All biological samples were collected following the biodiversity protocols and authorization from the Brazilian Institute of Renewable Natural Resources from the Ministry of the Environment.

Water

Surface water samples were collected in 26 stations around the area of influence of the Guamaré submarine outfalls (Fig. 1). Two stations were located within 50 m from the outfalls releasing point; eight and ten stations were distributed within a 500-m and within 2,000-m radius from the releasing points, respectively; whereas six stations were established outside a 4,000-m radius from the outfalls, being considered as control. This sampling grid has been used in other marine exploration sites with the farther stations also considered as controls (Kennicutt et al. 1996a; Gray et al. 1999; EPA 2000). Water column in this area is relatively shallow (5 to 20 m) and showed no stratification, however, bottom water samples were collected in selected seven stations, representing the four radius to check for eventual differences in metal content. Water samples were not collected at the outer shelf area; since earlier studies showed the signature of produced water discharge to disappear only a few meters from the platforms due to enormous dilution factors, up to 2,000 times in the first 10 to 100 m (Gabardo et al. 2005).

Samples were collected with Teflon lined Go-Flo bottles and transferred to pre-cleaned polyethylene bottles and kept under low temperature (~4 °C) until analysis. Acceptable clean protocols (Boutron 1990; Nriagu et al. 1993) were used throughout sampling, transport, and storage to avoid cross-contamination. Samples suffered no pre-treatment previous to analysis

and were analyzed unfiltered, therefore determining total (dissolved+particulate) metal content in the water.

The concentrations of Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn were performed by inductively coupled plasma mass spectrometry, after 20× sample dilution with ultrapure water using a Model X Series II spectrometer (Thermo Fisher Scientific, Bremen, Germany). Instrumental parameters were optimized for each element, in order to achieve the best instrumental signal to noise ratio. Pneumatic nebulization was used and the individual matrix matched calibration solutions ranged from 0.1 to 50 µg l⁻¹.

Mercury was determined by cold vapor atomic absorption spectrometry (CV AAS), using a home-made vapor generator accessory and a model RA 915⁺ Mercury Analyser (Lumex, St. Petersburg, Russia). In both cases, 50-ml aliquots were used.

Sediments

Surface sediment samples were collected in triplicate in the same 26 stations used for water samples plus 43 stations located in the continental shelf area under the influence of oil and gas production platforms. Samples were collected along four parallel lines including coastal samples up to 5 m deep, shallow shelf up to 50 m deep, shelf edge from 50 to 100 m deep and slope from 100 to 450 m deep (Fig. 2). Most samples were collected using a van Veen grab sampler, whereas in those stations closer to the submarine outfall, sediments were collected by divers using small steel cylinders. Based on a ten-sample comparison, no significant difference was found in metal concentrations in sediments when comparing the two sampling procedures. From the deeper sampling line (>100 m), a box corer was used to retrieve the samples. The samples were transferred to plastic bags, avoiding the contact with any metallic surface. Only the top 2.0 cm layer was used for metal analysis, irrespectively of the sampling device. Samples were kept frozen until analysis.

Previous to metals determination, approximately 100 g of oven dried (80 °C) sediments were used for gravimetric determination of the silt–clay fraction (<63 µ) through sieving. Whereas others aliquots (10 g) of dried sediment were used for gravimetric determination of total carbonates after reacting from 12 h with a 0.5 N HCl solution (Loring and Rantala 1992).

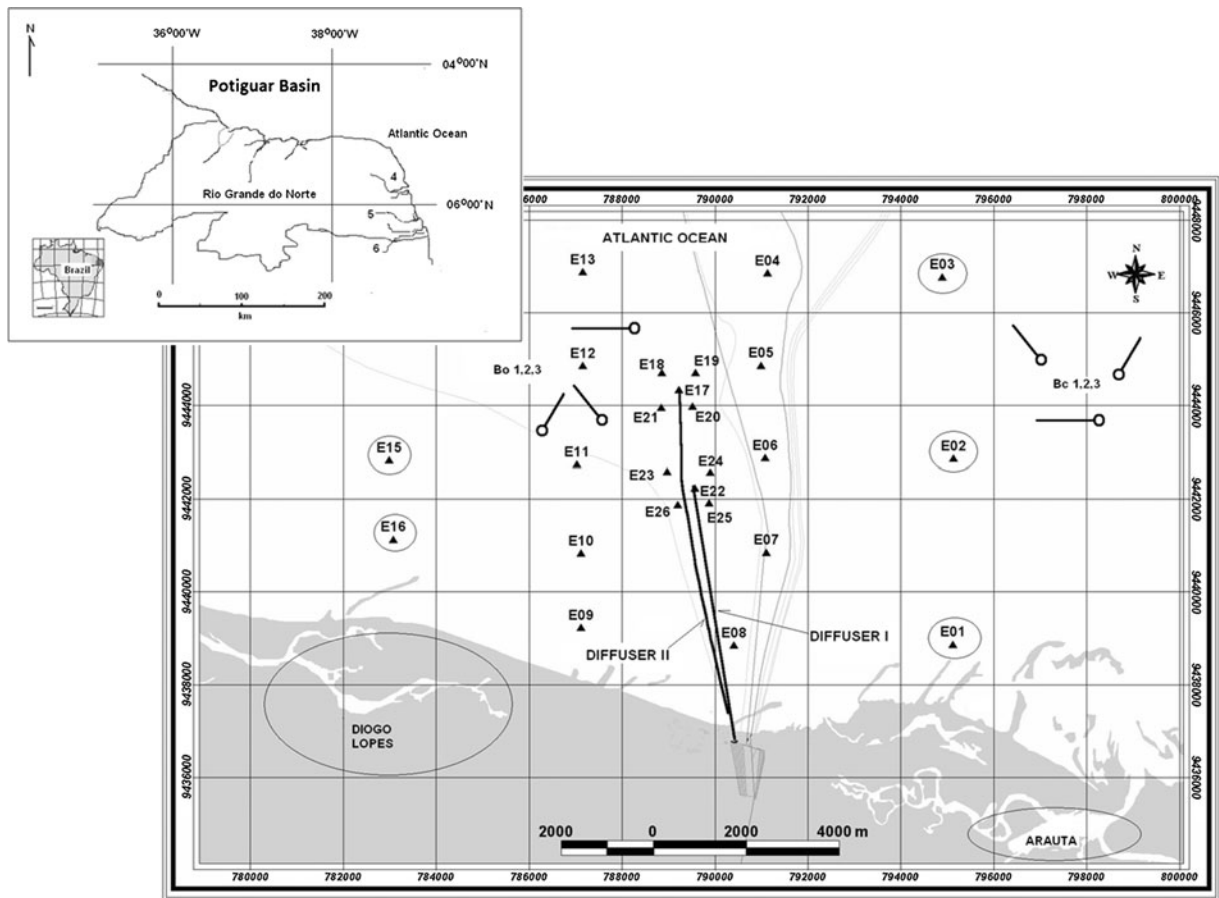


Fig. 1 Sampling sites surrounding the submarine outfalls of the Guararé water production treatment plant at the Potiguar Basin, NE Brazil: E1 to E26 are sampling sites for water ($n=26$) and bottom sediments ($n=26$); circled stations are those sampled for bottom and surface waters. Bo and Bc (—○) represents the location of the three sampling transects for trawlings of pbelagic

and benthic biota in the area under the influence of the Guararé submarine outfalls (Bo; $n=9$) and at a control site off Galinhos (Bc; $n=9$), respectively. Sampling areas for estuarine biota at Diogo Lopes ($n=9$) and Guararé ($n=7$) are circled. Geographic referencing system is UTM

Sediments for metal analysis were wet sieved and only the fraction <2.0 mm was used. The selection of this fraction allows the direct comparison of other monitoring programs on metal distribution in shelf sediments of Brazil (PETROBRAS [Petróleo Brasileiro S.A.] 2004a, b). For the determination of all elements but Hg, the samples (2 g) were accurately weighed in 50 ml screwed capped polypropylene tubes. The cups were just gently put onto the tubes and they were taken to a microwave oven at $110\text{ }^{\circ}\text{C}$, for 6 h. After cooling down to room temperature, they were weighed again. This procedure was repeated until a constant mass and the water content was determined. Previous tests have shown that the mass loss associated to the plastic tubes was negligible. This

procedure was preferred for a better contamination control.

Ten milliliters of sub-boiled HNO_3 were then added to each tube and kept in rest for 12 h. In continuation, the tubes were heated up to $70\text{ }^{\circ}\text{C}$ for 5 h, cooled and 1 ml of hydrogen peroxide was added and this solution was heated for 1 h more. In order to dissolve the silica residue, HF should have been added. However, due to the very high calcium content of the samples, the direct addition of HF led to the formation of insoluble CaF_2 . Thus the silica content was separated by centrifugation, the remaining solution was transferred to another tube and sub-boiled HF (1 ml) was added to the silica residue only, and gently heated. After silica dissolution, elimination of the HF excess by heating

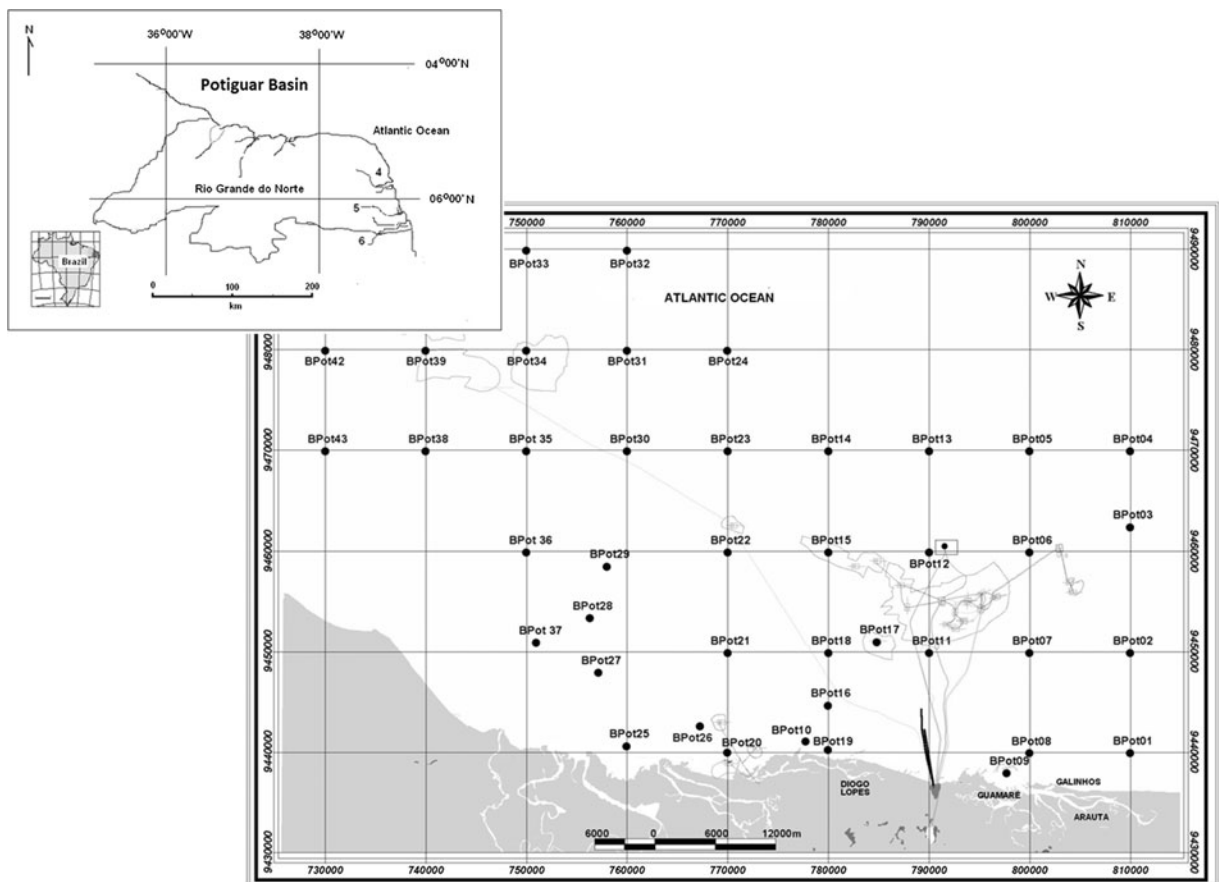


Fig. 2 Location of sampling sites (BPot 1 to 43) for bottom sediments at the continental shelf area under the influence of offshore oil and natural gas exploration at the Potiguar Basin, NE Brazil ($n=43$). Geographic referencing system is UTM

the digestate to dryness, and further redissolution. The two solutions were pooled and made up to 20 ml with ultrapure water. Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) with a Model Ultima 2 spectrometer (Jobin Yvon, Longjumeau, France), using pneumatic nebulization. The instrumental parameters were optimized for each element and individual external calibration ranging from 0.1 to 50 $\mu\text{g l}^{-1}$ was used for quantification.

For CVAAS mercury determination, the samples mass was 1 g, and the sample digestion performed using a 1+1 mixture of HNO_3 and H_2SO_4 but with lower temperature (60 °C). After sample dissolution, 5 % (m/v) KMnO_4 was added. Just before the instrumental analysis, the oxidant excess was reduced with 1 ml of a 20 % (m/v) hydroxylammonium chloride solution, the volume was made up to 20 ml with ultrapure water, and the tube was closed and centrifuged. Mercury was

determined in this solution after carefully pipetting 5 ml of this solution into the reaction flask of a MHS 10 vapor generator attached to a ContraAA Atomic Absorption Spectrometer (Analytik Jena, Jena, Germany) (Campos et al. 1993).

Biota

Benthic organisms from the Potiguar continental shelf were collected from stations distributed in two groups of three trawling transects. One located close to the emission releasing points of the submarine outfalls (Bo 1, 2, and 3) and the other in a control area (Bc 1, 2, and 3) located about 20–30 km from the outfalls transects, off Galinhos beach (Fig. 1). Trawling used a 15×7.5-m net with 3.4 cm of mesh aperture. Each trawling lasted for 30 min. Samples included mostly bivalves, crustaceans and fish. Sampling of the shelf biota was performed only in the last three campaigns in May 2003, November

Table 1 Comparison between surface and bottom water metal concentrations (total concentrations, dissolved+particulate in micrograms per liter) in selected stations at the Potiguar Basin (*n*=21)

Depth	Al	Fe	Ba	Mn	Ni	Zn	Cu
Bottom							
Mean	34±22	1.3±0.2	12±8	3±2	15±12	15±22	8±9
Range	17–65	1.1–1.4	<0.1–25	1–7	10–19	<1–48	<1–20
Surface							
Mean	22±20	1.4±0.3	23±27	4±1	9±7	12±18	7±9
Range	5–43	<1–1.8	7–89	3–8	3–27	2–39	2–20

2003, and July 2004. A single sampling campaign of estuarine organisms from Diogo Lopes and Arauta estuaries, under the influence of the Guamaré industrial center were also collected in one campaign in July 2004.

On board organisms were identified, measured and frozen for transport. In the laboratory, whole soft tissues of invertebrates were used for analysis, whereas for fish only muscle tissues were used. In order to achieve the minimum mass, organisms of the same size were pooled when necessary. The excess of water was dried by softly pressing the specimen with paper towels and the samples were macerated, transferred to plastic (zip lock) bags, and kept frozen until analysis (Francioni et al. 2004). For the determination of Cd, Cr, Cu, Ni, Pb, V, and Zn, 2 g subsamples were accurately weighed in 50-ml screwed capped polypropylene tubes. To each tube, 10 ml of sub-boiled HNO₃ were added and the tubes were transferred to a heating block at 80 °C and kept heated until complete sample dissolution. The samples were cooled down to room

temperature and further oxidation was performed by the addition of perhydrol. The samples were heated again for 2 h and made up to 50 ml with ultrapure water. The instrumental determination was performed by ICP-OES as described for the sediments analysis. For Hg determination, the samples were accurately weighed (0.5 g) in 50-ml screwed capped polypropylene tubes. To each tube, 10 ml of a 1+1 (v) mixture of HNO₃ and H₂SO₄ were added. After sample dissolution, 5 ml of 5 % (m/v) KMnO₄ were added. Mercury was determined in this solution by CV AAS, using a MHS 10 vapor generator attached to a ContrAA Atomic Absorption Spectrometer (Analytik Jena, Jena, Germany). Just before the instrumental analysis, the oxidant excess was reduced with a 10 % (m/v) hydroxylammonium chloride solution. External calibration was performed with aqueous calibration solutions.

All results are expressed on wet weight basis to be comparable with the Brazilian environmental limits form

Table 2 Total metal concentrations (average and range in micrograms per liter) in marine waters under the influence of the effluents from the submarine outfalls at Guamaré in the Potiguar Basin

Metal	Campaign I	Campaign II	Campaign III	Campaign IV	Legal limits
Al	54 (22–163)	52 (37–87)	43 (36–49)	n.a.	1,500
Fe	n.a.	1(<0.2–63)	43 (<0.2–171)	4 (<0.2–16)	300
Ba	7 (4–15)	8 (7–89)	6 (<1–7)	5 (<1–17)	1,000
Mn	3 (2–8)	1 (1–12)	2 (<1–8)	2 (1–2)	100
Cu	n.a.	2 (1–3)	2 (<1–3)	2 (<1–3)	5
Pb	2 (1–21)	2 (<1–3)	1(<1–2)	<1	10
Zn	65 (21–246)	2 (1–10)	34 (8–59)	2 (1–19)	90
Ni	7 (2–27)	2 (<1–2)	1 (<1–2)	<1	25

Legal concentrations limits from the Brazilian Ministry of the Environment (CONAMA and Meio Ambiente 2005). Metals Cr, V, Cd, and Hg presented concentrations below the detection limit of the analytical procedure of 1.0 µg l⁻¹, for Cr, V, and Cd and of 0.01 µg l⁻¹ for Hg *n.a.* not analyzed in a given campaign

metal concentrations in marine biota (ANVISA and de Vigilância Sanitária 1998).

Quality assurance and control

All glass and plastic ware was washed with a 5 % Extran solution, deionized water, and immersed in 10 % HNO_3 for at least 24 h. Before analysis, they were washed with deionized water, ultrapure water, and let dry in an oven, at 40 °C, protected from dust and contact with any

metallic surface. Sample manipulation also avoided contact with metallic surfaces, and plastic foils and nylon trays were thoroughly used. An exception occurred for the biota maceration, when a stainless steel blender was used. However, successive blending and analysis of the same sample assured that contamination, if occurred was negligible. All reagents were of analytical reagent grade and mineral acids were purified by sub boiling distillation using a Teflon^R still. One vessel procedures were preferred, avoiding contamination due

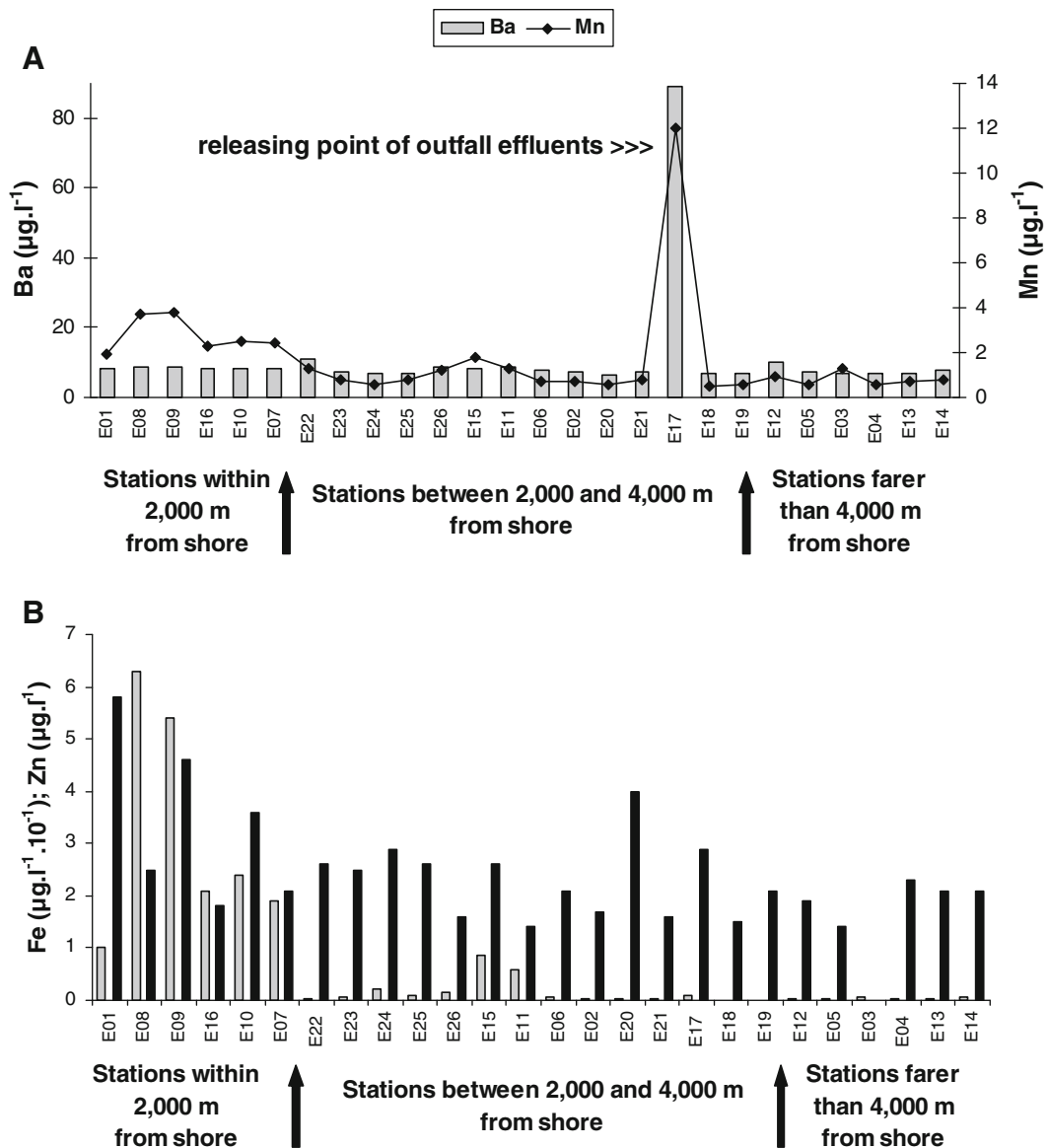


Fig. 3 Examples of spatial distribution of metal concentrations in waters in the area of influence of the Guamaré submarine outfalls. Figure 3a shows concentrations of Ba and Mn obtained

in the campaign II. Figure 3b shows Fe and Zn concentrations also from campaign II

to sample transferences and contact with multiple surfaces. Calibration solutions were prepared by adequate dilution of individual (Tritisol Merck, Darmstadt, Germany) or multi-elemental (Spex, Metuchen) 1,000 µgml⁻¹ standard solutions. Standard and sample solutions were manipulated in laminar flow hoods. A strict blank control protocol was followed and at least three blanks were present in each sample batch. Parallel analysis, in triplicate, of adequate certified references materials (MESS-2), “Marine Sediment Reference Materials for Trace Metals and other Constituents” from the National Research Council of Canada, and Buffalo River Sediment SRM 2704 from the National Institute of Standards and Technology (Gaithersburg) were also performed, and the obtained results were always within the ±5 % range (for Al, Fe, Hg, and Pb) and within the ±10 % range (for Cu, Zn, V, Cr, and Ni), in relation to

the certified values. All results are at least the average of triplicate samples.

For statistical analysis, nondetectable concentrations were posed equal to half the detection limit of the method.

Results and discussion

Metal distribution in waters

The comparison between metal concentrations in bottom and surface waters from selected seven stations in the area under the influence of the Guamaré outfalls, presented in Table 1, shows no significant difference (*P*<0.01) between the detectable elements suggesting completing mixing of the water column in this relatively (<20 m) shallow waters. Therefore, all results

Table 3 Metal concentrations (average and range in milligrams per gram for Al and Fe and micrograms per gram for the other elements) in marine sediments under the influence of the

effluents from the submarine outfalls at Guamaré and in the continental shelf at the Potiguar Basin

	Campaign I	Campaign II	Campaign III	Campaign IV
Guamaré				
Al	1.1 (0.2–3.3)	0.6 (0.2–6.5)	1.9 (0.9–12.2)	2.9 (0.9–7.0)
Fe	1.7 (0.6–4.3)	0.7(0.3–1.9)	1.2 (0.5–3.7)	1.3 (0.6–2.5)
Ba	61 (10–306)	19 (7–338)	48 (13–336)	270 (<2–831)
Mn	77 (25–166)	20 (2–38)	29 (10–107)	33 (12–74,8)
Cu	1.3 (0.6–4.6)	0.1 (<0.1–0.3)	0.7 (0.1–28)	0.6 (<0.1–4.3)
Pb	3.7 (1.2–10.5)	0.5(<0.1–4.5)	1.5 (0.2–4.8)	3.1 (0.7–8.0)
Zn	6.4 (0.8–26.5)	0.1 (<0.1–0.8)	1.9 (0.1–20)	1.2 (<0.2–6.3)
Ni	1.4 (0.97–5.1)	0.3 (0.1–0.8)	0.5 (0.2–2.4)	<0.1(<0.1)
Cr	7.9 (1.5–20.8)	3.4 (1.3–8.0)	4.5 (1.9–11)	4.7 (0.9–9.4)
V	5.8 (2.7–15.4)	4.5 (1.4–8.3)	3.2 (1.5–6.5)	3.4 (1.0–5.8)
Continental shelf				
Al	1.3 (0.2–5.0)	0.7 (0.1–13.4)	3.2 (0.4–26.3)	2.0 (0.1–22.2)
Fe	1.5 (0.3–6.9)	0.6 (0.1–7.1)	1.1 (0.2–7.1)	1.1 (0.2–19.8)
Ba	43 (3–503)	34 (6–332)	109 (7–700)	14 (<2–1,125)
Mn	60 (10–365)	16 (5–147)	27 (4–236)	23 (5–261)
Cu	1.3 (0.6– 6.2)	0.1 (<0.1–6.6)	0.3 (<0.1–2.1)	0.2 (<0.1–3.8)
Pb	4.2 (0.6–19)	0.4 (<0.1–7)	1.8 (0.1–12)	1.2 (<0.3–13)
Zn	3.1 (<0.1–36)	0.2 (<0.1–13)	1.5 (0.4–23)	1.2 (<0.2–20)
Ni	1.1 (<0.1–4.4)	0.2 (<0.1–7.0)	0.8 (0.2–7.5)	0.6 (<0.1–9.4)
Cr	6.6 (<0.1–25)	5.5 (2.4–23)	6.8 (3.1–31)	7.5 (5.6–24)
V	3.6 (0.3–17)	5.2 (2.1–40)	3.0 (0.6–54)	3.5 (5.8–43)

Metals Cd and Hg presented concentrations below the detection limit of the analytical procedure in over 75 % of the samples (LDs, 0.1 µgg⁻¹ for Cd and 0.001 µgg⁻¹ for Hg)

hereon presented can be assumed as representative of the entire water column.

Average and range of concentrations of metals measured in waters from the Guamaré outfalls influence area, in the four campaigns, are presented in Table 2. Of the 12 elements investigated, Hg, V, Cr, and Cd showed concentrations in all samples from all campaigns and stations below the detection limit of the methods used. On the other hand, concentrations of detectable elements were in general within the expected range of concentrations for noncontaminated coastal waters (Salomons and Forstner 1984) and below the Brazilian legal limits for metal concentrations in sea water (CONAMA and Meio Ambiente 2005).

The four sampling campaigns showed similar concentrations and spatial distribution for most metals. An exception was Zn with significantly higher peaks occurring in campaigns I and III and Fe in campaign III. Since water samples were analyzed without filtering, total metal concentrations may include dissolved and particulate species, it is possible then that these concentration

peaks represents events of resuspension or the presence of Zn- and Fe-enriched particles.

Spatial variability was observed within the individual campaigns. For elements particularly enriched in the submarine outfall effluents, such as Ba and Mn, concentrations showed peaks close to the effluent releasing point, as exemplified by the results from campaign II shown in Fig. 3a. Concentrations drop to natural values very close (<200 m) to the releasing point due to high dilution, as showed in other offshore exploitation areas (Brandsma and Smith 1996). Another typical spatial distribution pattern is that represented by those elements which are mostly of terrigenous origin, such as Fe and Zn, and to a lesser extent Al and Cu. These elements showed highest concentrations in stations closer to shore, as exemplified by the results from campaign II shown in Fig. 3b (see also Mn spatial distribution in Fig. 3a). In fact, continental contribution can be the single most important parameter in determining metal concentrations in continental shelf water (Freire et al. 2004; Lacerda and Marins 2006).

Table 4 Range of concentrations of Al, Fe, Ba, and trace metals in bottom sediments from the Potiguar basin compared with other sectors of the Brazilian continental shelf

Element	Inner continental shelf, SE Brazil ^{a, b}	Inner continental shelf, NE Brazil ^{c, d, e}	Outer campos basin, SE Brazil ^f	Inner outfall area, Potiguar Basin ^g	Outer shelf area, Potiguar Basin ^g
Al	8.6–31.4	0.18–1.7	6.8–10.6	0.6–2.9 (2.4)	0.1–26.3 (4.5)
Fe	6.1–16.4	2.5–8.6	5.8–6.9	0.7–1.7 (1.2)	0.6–19.8 (1.9)
Ba	112–124	–	165–188	19–270 (136)	<2–1,125 (124)
Mn	70–90	9–210	74–88	20–77 (29.4)	4–365 (38)
Cu	19–29	3–42	3.4–6.3	<0.1–28 (1.0)	<0.1–6.6 (0.6)
Pb	17–38	16–47	5.5–6.7	<0.1–10.7 (1.8)	<0.1–19.0 (2.4)
Zn	78–147	99–270	24.5–28.9	<0.1–26.5 (1.9)	<0.1–36.0 (2.7)
Ni	25–36	4–12	6.2–7.7	<0.1–5.1 (0.4)	<0.1–9.4 (1.3)
Cr	76–84	3–39	14–15	0.9–20.8 (4.4)	<0.1–31.0 (9.0)
V	6–51	–	15.7–17	1.0–15.4 (3.8)	0.3–54.0 (6.7)

Al and Fe in milligrams per gram dry weight; all other elements in micrograms per gram dry weight

^aCarvalho et al. (2002)

^bRezende et al. (2002)

^cFreire et al. (2004)

^dNascimento et al. (2010)

^eLacerda and Marins 2006

^fRezende et al. (2004)

^gRange of concentrations found for all campaigns; this study. Overall averages, $n=84$ for the outfall area; $n=138$ for the outer shelf area. Brazilian legal limits for sediments in micrograms per gram of dry sediment (CONAMA and Meio Ambiente 2004) for Cu=34; Pb=46.7; Zn=150; and Ni=20.9; no limits are established for Al, Fe, Ba, and Mn

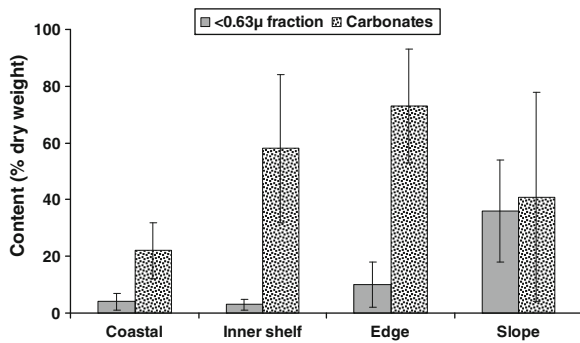
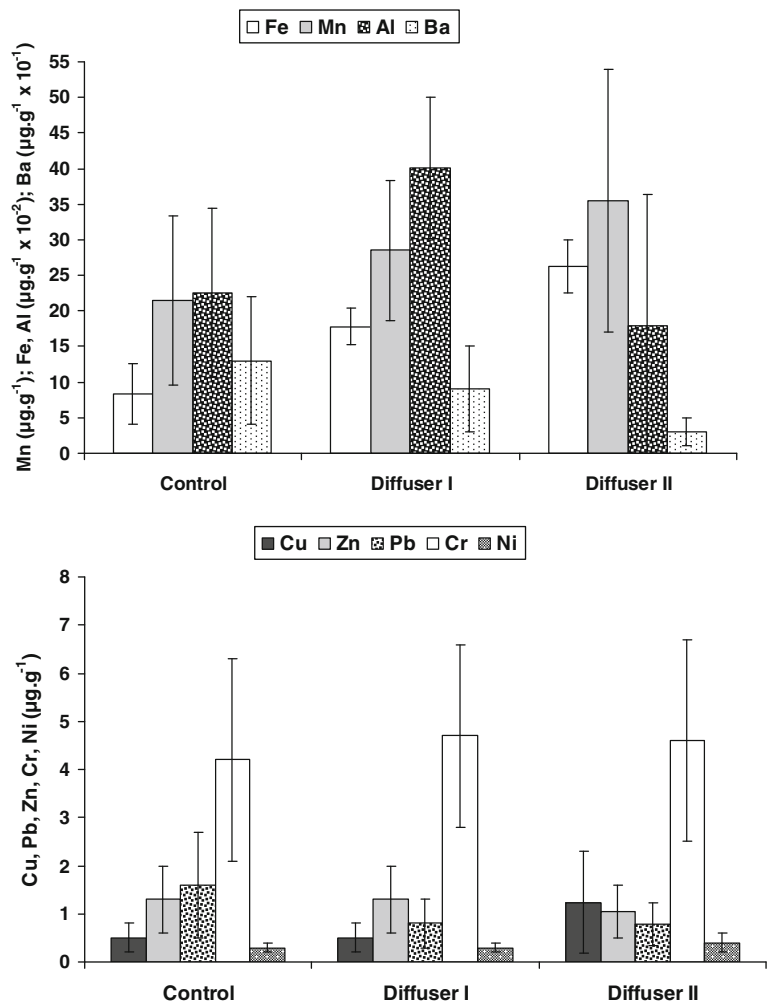


Fig. 4 Content and spatial distribution of carbonates and silt-clay fractions (<63 μm) in sediments from the continental shelf at the Potiguar Basin, NE Brazil

The continental signature virtually impair the detection of any metal contribution from effluents of offshore

oil and gas production as shown by Prego and Cobelo-Garcia (2003, 2004), during the monitoring program of the *Prestige* oil spill in the coast of Spain. Along the Norway coast, Johnsen et al. (2004) estimated that continental inputs of metals are from 2 to 5 orders of magnitude higher than the total amount associated with produced water release from offshore gas and oil exploration. In the Gulf of Mexico, the monitoring sampling grid of offshore oil and gas exploitation excludes those sectors under the influence of continental inputs associated with the Mississippi river plume (Kennicutt et al. 1996). At the Potiguar basin, even under a semi-arid climate, average continental fluxes reach about 200 m³ s⁻¹ (Ekau and Knoppers 1999), compared with an estimate flux of produced water ranging from 0.3 to 0.5 m³ s⁻¹. Therefore, the continental signature impedes the detection of any abnormality in metal concentrations

Fig. 5 Distribution of metal (Al, Ba, Mn, Fe, Cr, Ni, Pb, Cu, and Zn) concentrations in sediments from groups of sampling stations at three different sites in the area of influence of the Guamaré submarine outfalls



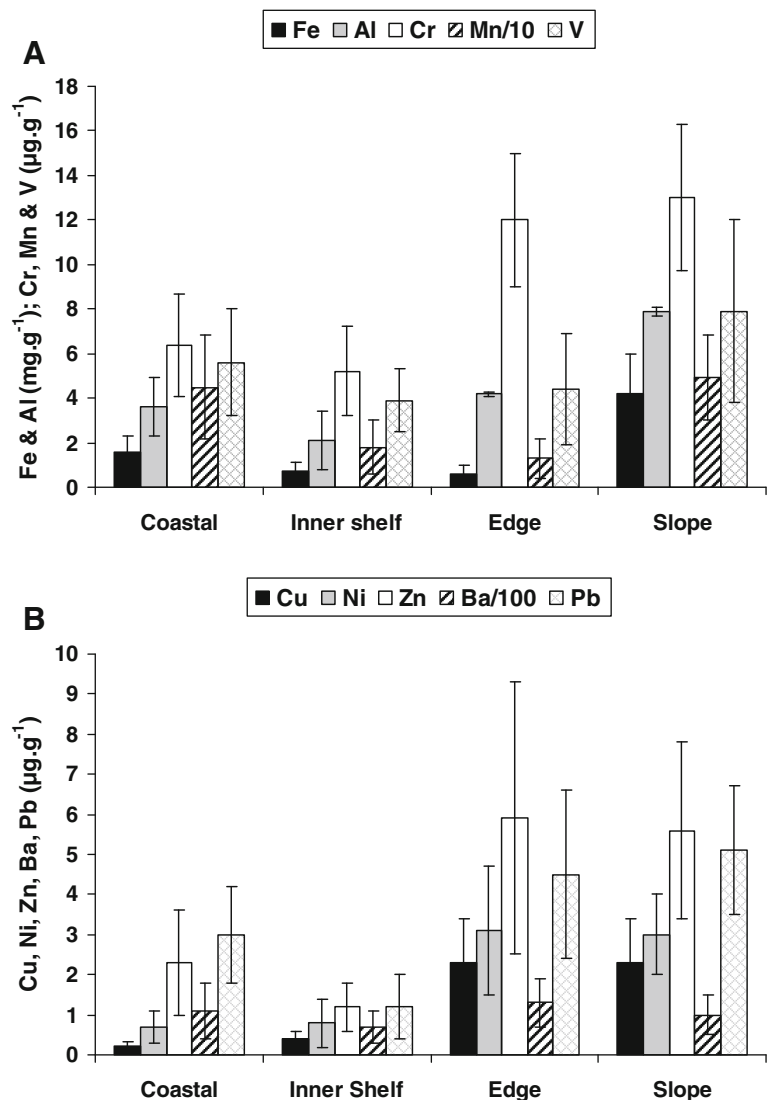
due to produced water, except in those stations located at the effluent releasing point proper and for Mn and Ba only.

Metal distribution and geochemistry in bottom sediments

Metal concentrations measured in bottom sediments from the area under the influence of the submarine outfall and from the broader continental shelf are presented in Table 3 for the four sampling campaigns. There was no significant difference of metal concentrations among sampling campaigns in both areas, mostly due to the relatively large variability of concentrations among

stations and campaigns. Concentrations followed the decreasing order of abundance: $Al \geq Fe > Ba \geq Mn > Cr > V > Zn > Pb > Ni \geq Cu > Cd > Hg$, in the four campaigns and, in general, for both areas. However, between the two sampling areas, concentrations of some metals (e.g., Cr, Cu, and V) were lower at the outfall area than in the outer shelf, particularly when the stations located in the edge of the shelf and the slope are considered, as will be further discussed. The high variability between stations and campaigns hampers the determination of any statistical significant difference among any element in the two areas. This variability seems typical to this sector of the Brazilian continental shelf due to the presence of scattered areas of relic sediments, and calcareous shale,

Fig. 6 Distribution of metal concentrations (Al, Ba, Mn, Fe, Cr, Ni, Pb, Cu, and Zn) in sediments from groups of sampling stations located in lines parallel to shore in continental shelf of the Potiguar Basin, NE Brazil



filling palaeo-canals, with random occurrence in the area. Also, the very nature of the NE Brazil shelf sediments, constituted by a mosaic of biogenic carbonates, both as detritus and living carbonate algae, sands, and fine sediments, contributes to the large variability in metal concentrations observed in bottom sediments (Martins and Coutinho 1981; Arz et al. 1999; Nascimento et al. 2010).

The metal concentrations found are within the range previously reported for sediments of the NE continental shelf of Brazil (Freire et al. 2004; Lacerda and Marins 2006; Nascimento et al. 2010) and in the lower range of values reported for the SE Brazilian continental shelf sediments (Carvalho et al. 2002; Rezende et al. 2004). Also for those metals regulated by legal limits (Cu, Pb, Zn, Hg, and Ni), all presented lower concentrations than those limits (CONAMA and Meio Ambiente 2004) (Table 4). This difference in trace metal concentrations between the two sectors of the Brazilian continental shelf has been previously reported as an effect of the more siliclastic nature of SE sediments compared with the mostly sandy and carbonate nature of the NE sector (Arz et al. 1999; Marins et al. 2004; Lacerda and Marins 2006). Whereas in the Potiguar basin, average silt–clay content ranged from <0.1 to 14 % in the outfalls and in the outer shelf areas, respectively; silt–clay content in the SE sector of the Brazilian coast are much higher, with average values varying from 36 to 56 %, in inner and outer shelf sediments (Lacerda et al. 2004). Also, silt–clay content is not only much higher in the SE sector (Milliman and Summerhayes 1975; Summerhayes et al. 1975; Lacerda and Marins 2006) but is also dominated by high cations exchange capacity smectite, compared with the lower exchange capacity caolinite, more abundant in sediments of the NE sector, which also contribute to the differences found in metal concentrations between the two sectors of the continental shelf (Muller et al. 1999).

An analysis of metal distribution in individual stations, similar to what was performed for water sampling station, showed, however, no significant contamination of the sediments by metals in stations closer to the outfalls effluents, when all samples are compared together. Also, a detailed analysis of only those stations surrounding the outfalls releasing points showed no significant difference between the concentrations of most metals found closer and farther from the releasing point. The only exceptions were Fe and Mn, which presented

significantly higher concentrations in the sampling stations located closer to the releasing points (Fig. 4), in particular close to the diffuser II, whose effluent is released in a single point, whereas from diffuser I effluents are dispersed through a pipeline of about 300 m. These results are in agreement with the anomalies observed in Mn concentrations in waters. However, probably due to the high and variable concentrations of Ba in the outfall area, the anomaly verified in water samples could not be detected in bottom sediments.

Considering the general range of concentrations from Table 3, it is also clear that no enrichment could be detected due to the oil exploration activities in the outer shelf area. On the other hand, clay and carbonate content and trace metal concentrations, present significant differences when stations are pooled according to their position in the shelf relative to the coast. Figure 5 shows the distribution of clay and carbonate fraction at the sampling area. Clay fraction average concentrations considering all stations among the four campaigns were low, ranging from 0.0 to 14.3 %. Higher values occurred at slope sampling sites (>100 m deep), followed by shelf edge sampling sites (50 to 100 m deep) and from those stations located in more shallow areas (≤5 m) close to shore. Carbonate average content was high in most stations ranging from 29 to 58 % with individual stations content ranging from 0.0 to 100 %. Highest values occurred at the depth

Table 5 Factor loadings (unrotated) from principal components analysis (entries (loadings) set in italics are >0.670) of geochemical variables in sediments from the Potiguar Basin, NE Brazil

Variable	Outfalls area		Shelf area	
	Factor 1	Factor 2	Factor 1	Factor 2
Fe	<i>0.933</i>	0.060	<i>-0.905</i>	0.295
Mn	<i>0.905</i>	0.002	<i>-0.923</i>	0.109
Al	<i>0.838</i>	-0.385	<i>-0.878</i>	-0.218
Ba	0.518	<i>-0.673</i>	-0.430	<i>-0.850</i>
V	0.436	0.010	<i>-0.867</i>	0.333
Cr	<i>0.759</i>	0.030	<i>-0.793</i>	0.158
Ni	<i>0.692</i>	0.381	<i>-0.786</i>	0.300
Cu	0.304	0.381	-0.508	-0.556
Zn	0.565	0.477	<i>-0.868</i>	0.201
Pb	0.630	<i>-0.693</i>	<i>-0.806</i>	-0.479
<63	0.481	0.625	-0.411	0.183
Carb	0.157	0.461	0.095	0.465

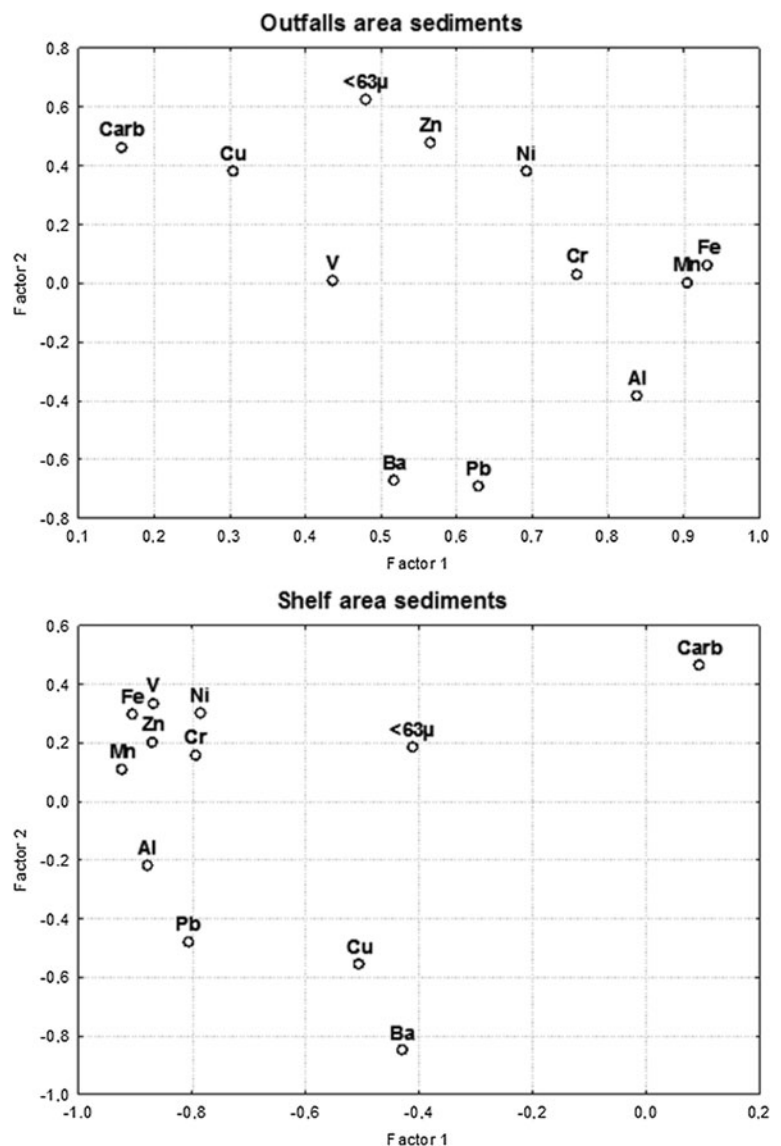
dominated by calcareous algae at the inner and edge sectors between 20 and 70 m deep (Fig. 5).

Figure 6 shows the spatial distribution of the studied metals in the four segments of the continental shelf. This distribution reflects well that of the clay content of the sediments. Concentration distribution for most metals were quite similar, decreasing from stations closer to shore to the inner shelf and increased steadily towards deeper stations at the edge and slope area of the continental shelf, generally following the distribution of fine particles of continental origin and suggesting a deposition are in deeper areas of the shelf. This distribution patterns has been recently

identified in other sectors of the Brazilian continental shelf and was also associated with increasing clay content in the deeper outer shelf sediments (Araujo et al. 2010).

Table 5 shows the unrotated factor loadings from a principal components analysis performed on the geochemical variables in the Potiguar Basin sediments. The results clearly show a factor 1, probably continental runoff inputs and represented not only mostly by Fe, Mn, and Al but also by Cr, V, and Ni in the outfalls area, and these metals plus Zn and Pb in the outer shelf, as responsible for most metal concentration variation. Factor 2 probably relates to internal shelf

Fig. 7 Two-dimensional plot of principal components analysis results on the distribution of geochemical variables in sediments from the Potiguar Basin, NE Brazil



processes, which may be associated with internal processes of the continental shelf influencing Ba, Cu, and Pb in the outfalls area and Ba in the outer shelf sediments, respectively. The distribution of Ba, however, outstands as unique among all variables analyzed, and this may suggest a different mechanism controlling its distribution in bottom sediments, which may be associated with anthropogenic sources (Fig. 7).

Previous studies on the geochemical controls of metal concentrations in bottom sediments of the Brazilian continental shelf suggests an important role of the continental contribution and of the influence of silt and clay contents of sediments (Rezende et al. 2004; Freire et al. 2004; Lacerda et al. 2004; Marins et al. 2004; Lacerda and Marins 2006). Continental

contribution to the SE Brazilian shelf, which is up to ten times higher than along the NE semi-arid littoral (Ekau and Knoppers 1999) can still be detected in slope sediments over 200 m deep (Lacerda et al. 2004; Araujo et al. 2010). Even under semi-arid conditions of the NE coast at the Potiguar Basin, continental runoff influence on metal concentrations can be also be identified even in the outer shelf sediments as suggested by the principal component analysis.

The large variability between campaigns and sampling areas hamper a robust correlation analysis between elements. Therefore, the correlation coefficients shown in Table 6 shall be viewed with care. However, the influence of the continental inputs is clearly shown, for example, by the significantly positive correlations ($P < 0.01$) found in

Table 6 Correlations between the studied elements in bottom sediments from the area of influence of the submarine outfalls ($n=21$) and from the outer continental shelf ($n=42$)

	Fe	Mn	Al	Ba	V	Cr	Ni	Cu	Zn	Pb	<63 μ	Carb
<i>n=21</i>												
Fe	1.000											
Mn	0.930*	1.000										
Al	0.737*	0.718*	1.000									
Ba	0.372	0.390	0.644*	1.000								
V	0.449*	0.452*	0.261	0.099	1.000							
Cr	0.658*	0.649*	0.639*	0.234	0.239	1.000						
Ni	0.661*	0.600*	0.424*	0.030	0.294	0.641*	1.000					
Cu	0.209	0.143	0.040	0.138	-0.010	0.062	0.147	1.000				
Zn	0.483*	0.409	0.250	0.136	0.070	0.285	0.418*	0.778*	1.000			
Pb	0.495*	0.513*	0.781*	0.839*	0.254	0.385	0.080	0.105	0.161	1.000		
<63 μ	0.470*	0.384	0.268	-0.089	-0.024	0.370	0.529*	0.232	0.523*	-0.151	1.000	
Carb	0.146	0.214	-0.045	-0.187	0.419*	0.060	0.107	0.115	0.117	-0.151	0.245	1.000
<i>n=42</i>												
Fe	1.000											
Mn	0.904*	1.000										
Al	0.706*	0.765*	1.000									
Ba	0.110	0.289	0.551*	1.000								
V	0.956*	0.873*	0.638*	0.083	1.000							
Cr	0.684*	0.609*	0.690*	0.262	0.658*	1.000						
Ni	0.722*	0.690*	0.621*	0.060	0.694*	0.793*	1.000					
Cu	0.288	0.346*	0.454*	0.646*	0.244	0.301	0.290	1.000				
Zn	0.855*	0.852*	0.672*	0.187	0.834*	0.612*	0.641	0.347*	1.000			
Pb	0.583*	0.722*	0.849*	0.795*	0.555*	0.546*	0.439	0.517*	0.569*	1.000		
<63 μ	0.348*	0.334*	0.277	0.038	0.270	0.305*	0.346	0.219	0.390*	0.207	1.000	
Carb	-0.037	-0.090	-0.128	-0.258	0.027	0.095	-0.005	-0.143	-0.058	-0.215	0.051	1.000

* $P < 0.05$, significant correlations

all campaigns and sampling sites between Fe, Al, Mn, Ni, and Cr. These five elements are typically originated from terrigenous sources and have been identified as having their distribution controlled by the distribution of the continental inputs from the continent (Carvalho et al. 2002; Freire et al. 2004; Rezende et al. 2004; Lacerda and Marins 2006; Aguiar et al. 2007). The other metals present different correlations among them and with the five terrigenous elements depending on the sampling area. In the area closer to the submarine outfall, very high sand content in many samples results in extremely variable concentrations of Pb, Zn, Cu, and V, including many stations with concentrations below the detection limits of the methods used. Therefore, these four metals do not present any characteristic pattern of correlation among them and with the terrigenous metals (Table 6). Through the outer continental shelf, however, higher silt and clay content and a significant decrease of sands result in strong correlation between all metals with the five typically terrigenous elements and among themselves (Table 6). The only element not correlated with any other metal is

Ba, in agreement with the factor analysis, suggesting different mechanisms controlling its spatial distribution in the Potiguar Basin sediments. This element is enriched and ubiquitous in various effluents from prospecting and exploration of offshore oil and gas reserves (Neff 2002). It is also particularly abundant in produced waters (Gabardo et al. 2005) therefore; its distribution in bottom sediments of the Potiguar Basin may be a result of anthropogenic inputs rather than natural distribution.

Lacerda and Marins (2006) have highlighted the importance of carbonate coprecipitation in influencing the spatial distribution of some metals (Cu, Zn, and Pb), in condimental shelf sediments off the Ceará coast, adjacent to the Potiguar Basin. Unfortunately, the low concentrations of these metals in our study area make difficult any discussion about the eventual role played by carbonates. In fact no significant correlation, except with V in the outfalls area ($r=0.419$; $P<0.05$), between the studied elements and carbonates were ever found in sediments of the Potiguar Basin, contrary to other sectors of the Brazilian continental

Table 7 Metal concentrations (in micrograms per gram wet weight) in shellfish species sampled at Diogo Lopes and Aratú estuaries at the Potiguar Basin, Northeastern Brazil (average concentration and range)

	Cd	Cr	Cu	Ni	Pb	V	Zn	Hg
Diogo Lopes Estuary								
<i>Anomalocardia</i>	<0.01	0.13	0.18	0.10	0.23	<0.01	0.57	0.008
<i>brasiliiana</i>	–	0.02–0.42	<0.05–0.39	<0.01–0.30	<0.03–0.24	<0.01–0.02	0.16–1.90	0.003–0.01
(n=5)								
<i>Mytella guayanensis</i>	<0.01	0.61	0.83	1.09	<0.03	0.03	5.4	0.008
(n=4)	–	0.28–1.80	0.49–1.30	0.53–2.20	–	<0.01–0.09	2.8–7.9	0.002–0.01
<i>Crassostraea</i>	0.07	0.50	3.4	0.37	0.12	0.03	70.6	0.005
<i>rhizophora</i>	0.04–0.1	0.18–0.75	2.5–5.0	0.21–0.54	0.06–0.17	<0.01–0.04	58–88	0.003–0.008
(n=4)								
<i>Callinectes</i> sp.	<0.01	0.37	10.9	0.19	<0.03	0.02	8.40	0.016
(composite sample)								
Aratú River Estuary								
<i>A. brasiliiana</i>	<0.01	0.04	0.06	0.03	<0.03	<0.01	0.39	0.008
(n=5)	–	0.03–0.06	<0.05–0.07	0.03–0.05	–	–	0.46–0.48	0.008–0.01
<i>M. guayanensis</i>	<0.01	0.48	0.95	0.93	<0.03	<0.01	6.0	0.005
(n=4)	–	0.21–0.76	0.84–1.1	0.93–0.94	–	–	5.5–6.5	0.005–0.006
<i>C. rhizophora</i>	0.02	0.10	0.09	0.12	0.03	–	25.4	0.004
(n=4)	<0.01–0.04	0.02–0.27	<0.01–0.27	<0.01–0.22	<0.03–0.05		0.6–82	<0.001–0.01
<i>Callinectes</i> sp.	<0.01	0.79	8.50	0.41	<0.03	0.04	9.60	0.012
(composite sample)								
Legal concentration	1.0	–	30	5	2	–	50	0.5
limits (ANVISA and de								
Vigilância Sanitária 1998)								

Legal concentrations limits from the Brazilian Ministry of Health (ANVISA and de Vigilância Sanitária 1998)

shelf. The principal factor analysis, however, also suggest a minor control of Cu and Zn, at least in the outfalls area, by carbonate precipitation. On the other hand, the presence of calcareous shale in the Potiguar Basin may mask the actual role of carbonate precipitation to the high content of clays in this mineralogy.

Metal distribution in the Potiguar basin biota

Table 7 shows the average metal concentrations in animals collected in the two estuarine areas monitored in the Potiguar Basin. Metals Cd, Pb, and V presented nondetectable concentrations in nearly all samples from both areas. Highest concentrations were of Zn found in oysters (*C. rhizophorae*), followed by the blue crab *Callinectes* sp. and by the mangrove mussel *Mytella guayanensis* and the cockle *Anomalocardia brasiliiana* (Table 7). Highest concentrations of Ni were found in the mussels, whereas Hg and Cu concentrations were highest in the blue crab. However, the small number of

individuals sampled in both areas and the large variability found within each species and metal hamper to estimate any statistically significant difference between the biota of the two areas.

All concentrations for all organisms and metals are well below the Brazilian legal maximum allowed concentrations for human consumption (ANVISA and de Vigilância Sanitária 1998). When compared with other estuarine areas along the Brazilian coast, concentrations are much lower than the values reported for industrialized and/or urbanized areas in the north and southeast coast characterized as moderately to heavily contaminated by metals, respectively, such as the São Luis Island, Maranhão State (Juras 1988); Sepetiba and Guanabara Bays, Rio de Janeiro State (Carvalho et al. 1993; Lacerda and Molisani 2006); Campos Basin, northern coast of Rio de Janeiro (Carvalho et al. 2001); Santos estuary, São Paulo State; and Botafogo River Estuary, Pernambuco State (Companhia de Tecnologia de Saneamento Ambiental 1981). Concentrations at the lower range of those reported for other noncontaminated areas in NE

Table 8 Metal concentrations (average of three samples in duplicate; in micrograms per gram wet weight) in fish species sampled close to the submarine outfalls and in a control area in the Potiguar Basin, northeastern Brazil

	Cd	Cr	Cu	Ni	Pb	V	Zn	Hg
Outfalls area								
<i>Rhinobatos percellens</i>	<0.01	0.05	0.10	<0.01	0.10	<0.01	1.05	0.112
<i>Diplectrum formosum</i>	<0.01	<0.01	<0.01	<0.01	<0.03	<0.01	0.044	0.033
<i>Syacium micrurum</i>	<0.01	0.02	<0.01	<0.01	<0.03	<0.01	0.046	0.017
<i>Bothus ocelladus</i>	<0.01	<0.01	<0.01	<0.01	0.27	<0.01	0.03	0.012
<i>Chaetodipterus faber</i>	<0.01	<0.01	<0.01	<0.01	0.26	<0.01	0.075	0.026
<i>Orthopristis ruber</i>	<0.01	0.02	<0.01	<0.01	0.28	<0.01	0.097	0.090
<i>Synodus intermedius</i>	<0.01	<0.01	<0.01	<0.01	0.28	<0.01	0.10	0.047
<i>Trinectes microphthalmus</i>	<0.01	0.09	<0.01	0.035	<0.03	<0.01	0.12	0.026
<i>Prionotus punctatus</i>	<0.01	<0.01	<0.01	<0.01	<0.03	<0.01	0.058	0.017
<i>Trachinocephalus myops</i>	<0.01	<0.01	<0.01	<0.01	<0.03	<0.01	0.009	0.017
<i>Dactylopterus volitans</i>	<0.01	0.02	<0.01	<0.01	<0.03	<0.01	0.11	0.016
Control area								
<i>R. percellens</i>	<0.01	0.16	0.16	0.06	<0.03	<0.01	1.2	0.459
<i>D. formosum</i>	<0.01	<0.01	<0.01	<0.01	<0.03	<0.01	0.013	0.020
<i>S. micrurum</i>	<0.01	<0.01	<0.01	<0.01	<0.03	<0.01	0.036	0.014
<i>Pomadasys covaeniformis</i>	<0.01	<0.01	<0.01	<0.01	<0.03	<0.01	0.056	0.024
<i>Lutjanus analis</i>	<0.01	<0.01	<0.01	<0.01	<0.03	<0.01	0.056	0.059
<i>Eucinostomus argenteus</i>	<0.01	<0.01	<0.01	<0.01	<0.03	<0.01	0.090	0.024
<i>Lutjanus synagris</i>	<0.01	0.02	<0.01	<0.01	<0.03	<0.01	0.031	0.021
<i>Haemulon plumieri</i>	<0.01	<0.01	<0.01	<0.01	<0.03	<0.01	0.034	0.085
Legal concentration limits (ANVISA and de Vigilância Sanitária 1998)	1.0	–	30	5	2	–	50	0.5

Brazil such as the Potengi estuary, at the Natal metropolitan area (Silva et al. 2001); the Curimataú estuary (Silva et al. 2003) both in Rio Grande do Norte State; and rivers along the Ceará state coast (Vaisman et al. 2005).

Metal concentrations measured in fish tissues from the continental shelf area influenced by effluents from the industrial park of Guamaré and from a control area far from the outfalls effluent releasing point (Fig. 1) are presented in Table 8. There was no significant difference between metal concentrations from the different species or sampling area. The only exception is Hg with significant higher concentrations in the carnivorous ray *Rhinobatos percellens* than in the other species, in particular in the specimens collected in the control area. Relatively high concentrations of Hg in offshore populations of carnivorous fish have been previously reported for the NE coast of Brazil (Lacerda et al. 2007). Concentrations for all metals, including Hg, and species are within the range reported for pristine environments and lower than those reported for even slightly contaminated areas along the Brazilian coast (Companhia de Tecnologia de Saneamento Ambiental 1981; Carvalho et al. 2000).

The results, although still preliminary since no other study on metal contamination in the area is available for comparison, suggest that concentrations of all metals and organisms are within the expected range for pristine environments, no influence of the exploration activity, or the releasing of effluents by the submarine outfalls could be detected. This is in agreement with results from monitoring programs of offshore oil and natural gas production or influenced areas in the world, such as the Persian Gulf (de Mora et al. 2004), the North Sea (Ruus et al. 2006; OOC [Offshore Operators Committee] 1997), the Gulf of Thailand (Windom and Crammer 1998), and the Straits of Malacca, in Malaysia (Agusa et al. 2004), where surveys failed to show increased metal contents in the biota due to these activities. Therefore, our results suggest that natural sources are still the major contributors of metals to the marine biota.

Conclusions

The results presented here showed no significant contamination of water, sediments, or biota by metals in the Potiguar Basin due to the influence of offshore oil and gas exploration. Most of the values found were in the

range expected for coastal and oceanic waters under pristine conditions. In few stations closer to the effluent releasing point from the submarine outfalls, anomalies in water and sediments were found for Ba, Fe, and Mn but restricted to the nearest stations, suggesting rapid dilution of metals present in effluents. On the other hand, differences in concentrations among group of stations were evident and influenced mostly by the continental contribution to the shelf and once there, by the distribution of continental material deposited in shelf sediments. Monitoring of the effects of the offshore oil and natural gas exploration needs to take into consideration the continental inputs, even in areas such as the Potiguar basin where, due to semi-arid conditions, continental inputs are small. On the other hand, the relatively short history of the activity in the Potiguar Basin (less than 20 years) and the chronic nature of the eventual exposure of the biota to pollutants derived from the exploration and treatment processes require the continuation of monitoring programs, in particular by studying long-term integrator compartments, such as sediment cores in selected low energy sites in the continental shelf and long-lived benthic biota.

Acknowledgments This work is part of the long-term monitoring program of Petróleo Brasileiro S.A. (PETROBRAS) of the offshore exploration areas at the Potiguar Basin. Thanks are also due to National Research Council of Brazil (CNPq; Proc. No. 573.601/2008-9) for providing grants and funding to the authors. The authors wish to thank PETROBRAS S.A. for allowing publication of part of the results and are particularly indebted to the crews of *N/RB Astro Garoupa* from PETROBRAS S.A. and from the *NOc Professor Martins Filho*, from the Federal University of Ceará, for the exhaustive logistic support during the monitoring program. The authors extend their thanks to two anonymous reviewers who kindly reviewed, detailed, and improved an earlier version of this manuscript.

References

- Aguiar, J. E., Marins, R. V., & Almeida, M. D. (2007). Comparação de metodologias de digestão de sedimentos marinhos para caracterização da geoquímica de metais-traço na plataforma continental nordeste oriental brasileira. *Geochimica Brasiliensis*, 21, 304–323.
- Agusa, T., Kunito, T., Vasunaga, G., Iwata, H., Subramanian, A., Ismail, A., & Tanabe, S. (2004). Concentrations of trace elements in marine fish and its risk assessment in Malaysia. *Marine Pollution Bulletin*, 51, 896–911.
- ANVISA, Agência Nacional de Vigilância Sanitária (1998). Portaria nº 685 de 27 de Agosto de 1998. Available at: <http://e-legis.anvisa.gov.br/leisref/public/showAct.php?id=90&word=alimentos>. Accessed 20 June 2010

- Araujo, B. A., Almeida, M. G., Salomão, M. S. M. B., Gobo, R. R., Siqueira, V. C., Ovalle, A. R. C., & Rezende, C. E. (2010). Distribuição de Hg total e suas associações com diferentes suportes geoquímicos em sedimentos marinhos da margem continental brasileira: Bacia de Campos-Rio de Janeiro. *Química Nova*, 33, 501–507.
- Arz, H. W., Patzold, G., & Wefer, G. (1999). Climatic changes during the last glaciation recorded in sediment cores from the northeastern Brazilian Continental Margin. *Geo-Marine Letters*, 19, 209–218.
- Boutron, C. F. (1990). A clean laboratory for ultralow concentration heavy metal analysis. *Fresenius' Journal of Analytical Chemistry*, 337, 482–491.
- Brandsma, M. G., & Smith, J. P. (1996). Dispersion modeling perspectives on the environmental fate of produced water discharges. In M. Reed & M. Johnson (Eds.), *Produced water 2: environmental issues and mitigation technology* (pp. 215–224). New York: Plenum Press.
- Campos, R. C., Resende, M. C. R., & Curtius, A. J. (1993). Application of the cold vapor technique to the speciation of mercury in fish samples after solvent extraction and methylmercury reduction directly in the organic medium. *Journal Analytical Atomic Absorption Spectrometry*, 8, 247–251.
- Carvalho, C. E. V., Faria, V. V., Cavalcante, M. P. O., Gomes, M. P., & Rezende, C. E. (2000). Distribuição de metais pesados em peixes costeiros bentônicos da região de Macaé, Estado do Rio de Janeiro, Brasil. *Ecotoxicology and Environmental Restoration*, 3, 64–68.
- Carvalho, C. E. V., Faria, V. V., Cavalcante, M. P. O., Gomes, M. P., & Rezende, C. E. (2001). Distribuição de metais pesados em mexilhões (*Perna perna*, L.) da Ilha de Santana, Macaé-Estado do Rio de Janeiro, Brasil. *Ecotoxicology and Environmental Restoration*, 4, 1–5.
- Carvalho, C. E. V., Salomão, M. S. M. B., Molisani, M. M., Rezende, C. E., & Lacerda, L. D. (2002). Contribution of a medium-size tropical river to the particulate heavy-metal load for the South Atlantic Ocean. *The Science of the Total Environment*, 284, 85–93.
- Carvalho, C. E., Gomes, M. P., & Lacerda, L. D. (1993). Heavy metal contamination of the marine biota along the Rio de Janeiro coast, SE-Brazil. *Water, Air, and Soil Pollution*, 57, 645–653.
- Companhia de Tecnologia de Saneamento Ambiental. (1981). *Estudo de mercúrio nas águas e estuário do Rio Botafogo—Pernambuco—1981. Fase I—Estudo preliminar* (p. 39). São Paulo: CETESB.
- CONAMA, Conselho Nacional do Meio Ambiente (2004). *Resolução n. 344, de 25 de Março de 2004. Dredging Sediments Limits*. Available in: <http://www.mma.gov.br/port/conama/res/res04/res34404.xml> Accessed on 03 September, 2011.
- CONAMA, Conselho Nacional do Meio Ambiente (2005). *Resolução n. 357, de 2005. Classificação dos corpos d'água*. Available in: <http://www.mma.gov.br/port/conama/res/res05/res35705.pdf> Accessed on 03 September, 2011.
- Crossland, C. J., Kremer, H. H., Lindeboom, H. J., Marshall-Crossland, J. I., & Le Tissier, M. D. A. (2005). *Coastal fluxes in the Anthropocene* (p. 231). Berlin: Springer.
- de Mora, S., Fowler, S. W., Wyse, E., & Azemard, S. (2004). Distribution of heavy metals in marine bivalves, fish and coastal sediments in the Persian Gulf and Gulf of Oman. *Marine Pollution Bulletin*, 49, 410–424.
- Ekau, W., & Knoppers, B. A. (1999). Sedimentation processes and productivity in the continental shelf of east and northeast Brazil. *Archives of Fisheries and Marine Research*, 47, 109–140.
- EPA. U.S. Environmental Protection Agency. (2000). *Environmental assessment of final effluent limitations guidelines and standards for synthetic-based drilling fluids and other non-aqueous drilling fluids in the oil and gas extraction point source category. EPA 821-B-00-014* (p. 266). Washington: EPA Office of Water.
- Francioni, E., Wagener, A. L. R., Calixto, R. C., & Bastos, G. C. (2004). Evaluation of *Perna perna* (Linné, 1758) as a tool to monitoring trace metals contamination in estuarine and coastal waters of Rio de Janeiro, Brazil. *Journal of the Brazilian Chemical Society*, 15, 103–110.
- Freire, G. S. S., Lima, S., Maia, L. P., & Lacerda, L. D. (2004). Geochemistry of continental shelf sediments of the Ceará coast, NE Brazil. In *Environmental geochemistry in tropical and subtropical environments* (pp. 365–378). Berlin: Springer.
- Gabardo, I. T., Platte, E. D., Lima, E. F. A., & Andrade, F. B. (2005). Caracterização do Efluente da Plataforma Curimã (PCR-1). In *Relatório Técnico Parcial, RTAMA 024/2005* (p. 47). Rio de Janeiro: CENPES.
- Gray, J. S., Bakke, T., Beck, H. J., & Nilssen, I. (1999). Managing the environmental effects of Norwegian oil and gas industry: from conflict to consensus. *Marine Pollution Bulletin*, 38, 525–530.
- Haynes, D., & Johnson, J. E. (2000). Organochlorine, heavy metal and polyaromatic hydrocarbon pollutant concentrations in the Great Barrier Reef (Australia) environment: a review. *Marine Pollution Bulletin*, 41, 267–278.
- Haynes, D., Leeder, J., & Rayment, P. (1997). A comparison of the bivalve species *Donax deltoideus* and *Mytilus edulis* as monitors of metal exposure from effluent discharges along the Ninety Mile Beach, Victoria, Australia. *Marine Pollution Bulletin*, 34, 326–331.
- Hübner, R., Astin, K. B., & Herbert, R. J. H. (2010). Dispersal and mobility of metal contamination across a salt marsh from coastal landfill sites using ammonium nitrate extractions as an indicator. *Journal of Environmental Monitoring*, 12, 740–747.
- Johnsen, J., Utvik, T. I. R., Garland, E., De Vals, B., & Campbell, J. (2004). *Environmental fate of contaminants in produced water. The Swedish SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production* (p. 9). Calgary: Society of Petroleum Engineers. SPE 86708.
- Juras, A. A. (1988). A preliminary survey of heavy metal concentrations in some estuarine organisms in the littoral zone of São Luis Island, Maranhão, Brazil. In U. Seeliger, L. D. Lacerda, & S. R. Patchineelam (Eds.), *Metals in Coastal Environments of Latin America* (pp. 16–20). Berlin: Springer Verlag.
- Kennicutt, M. C., Boothe, P. N., Wade, T. L., Sweet, S. T., Rezack, R., Kelly, F. J., Brooks, J. M., Presley, B. J., & Wisenburg, D. A. (1996). Geochemical patterns in sediments near offshore production platforms. *Canadian Journal of Aquatic Sciences*, 53, 2540–2553.

- Kennicutt, M. C., Green, R. H., Montagna, P. A., & Roscigno, P. F. (1996). Gulf of Mexico offshore operations monitoring experiment (GOOMEX). Phase I: sub-lethal responses to contaminant exposure—introduction and overview. *Canadian Journal of Aquatic Sciences*, 53, 2540–2553.
- Knoppers, B. A., Ekau, W., & Figueiredo, A. G. (1999). The coast and shelf of east and northeast Brazil and material transport. *Geo-Marine Letters*, 19, 171–178.
- Lacerda, L. D., & Molisani, M. M. (2006). Three decades of Cd and Zn contamination in Sepetiba bay, SE Brazil evidence from the mangrove oyster *Crassostrea rhizophorae*. *Marine Pollution Bulletin*, 52, 974–977.
- Lacerda, L. D., & Marins, R. V. (2006). Geoquímica de sedimentos e o monitoramento de metais na plataforma continental Nordeste Oriental do Brasil. *Geochimica Brasiliensis*, 20, 123–135.
- Lacerda, L. D., Rezende, C. E., Carvalho, C. E. V., Ovalle, A. R. C., & Pfeiffer, W. C. (1993). Mercury distribution in sediments of the Paraíba do Sul River Estuary, SE Brazil. *Marine Pollution Bulletin*, 20, 93–96.
- Lacerda, L. D., Rezende, C. E., Ovalle, A. R., & Carvalho, C. E. (2004). Mercury distribution in continental shelf sediments from two offshore oil fields in southeastern Brazil. *Bulletin of Environmental Contamination and Toxicology*, 72, 178–185.
- Lacerda, L. D., Santos, J. A., Campos, R. C., Gonçalves, R. A., & Salles, R. (2007). Total-Hg and organic-Hg in *Cephalopholis fulva* (Linnaeus, 1758) from inshore and offshore waters of NE Brazil. *Brazilian Journal of Biology*, 67, 493–498.
- Loring, D. H., & Rantala, R. T. T. (1992). Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth-Science Reviews*, 32, 235–283.
- Marcovecchio, J. E. (2000). *Overview on land-based sources and activities affecting the marine, coastal and associated freshwater environment in the Upper Southwest Atlantic Ocean*. UNEP Regional Seas Reports and Studies No. 170, The Hague: UNEP/GPA. 78 p.
- Marins, R. V., Lacerda, L. D., Parauetti, H. H. M., Paiva, E. C., & Villas Boas, R. C. (1998). Geochemistry of mercury in sediments of a sub-tropical coastal lagoon, Sepetiba Bay, southeastern Brazil. *Bulletin of Environmental Contamination and Toxicology*, 61, 57–64.
- Marins, R. V., Paula Filho, F. J., Lacerda, L. D., Rodrigues, S. R., & Marques, W. S. (2004). Distribuição de mercúrio total como indicador de poluição urbana e industrial na costa brasileira. *Química Nova*, 27, 763–770.
- Martins, L. R., & Coutinho, P. N. (1981). The Brazilian continental margin. *Earth Sciences Reviews*, 17, 87–107.
- Milliman, J. D., & Summerhayes, C. P. (1975). Upper continental margin sedimentation off Brazil. *Contributions to Sedimentology*, 4, 1–43.
- Molisani, M. M., Salomão, M. S. M. B., Ovalle, A. R. C., Rezende, C. E., Lacerda, L. D., & Carvalho, C. E. V. (1999). Heavy metals in sediments of the lower Paraíba do Sul River and estuary, Southeastern Brazil. *Bulletin of Environmental Contamination and Toxicology*, 63, 682–690.
- Muller, G. G., Irion, G., Morais, J. O. & 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 (p. 1–4). In: Abrão, J.J. (ed) *Proceedings of the 3rd International Symposium on Environmental Geochemistry in Tropical Countries*. Niterói: Universidade Federal Fluminense
- Nascimento, F. S., Freire, G. S. S., & Miola, B. (2010). Geochemistry of marine sediments of the Brazilian Northeastern continental shelf. *Brazilian Journal of Oceanography*, 58, 1–11.
- Neff, J. M. (2002). *Bioaccumulation in marine organisms: effect of contaminants from oil well produced water* (p. 452). Duxbury: Battelle Coastal Resources and Environmental Management.
- Nriagu, J. O., Lawson, G., Wong, H. K. T., & Azcue, J. M. (1993). A protocol for minimizing contamination in the analysis of trace metals in Great Lakes waters. *Journal of the Great Lakes Research*, 19, 175–182.
- OGP. (2005). *Fate and effects of naturally occurring substances in produced water on the marine environment* (p. 36). London: The International Association of Oil and Gas Producers. Report 364.
- OOO [Offshore Operators Committee]. (1997). Gulf of Mexico produced water bioaccumulation study. Definitive component. In *Technical report to the offshore operators committee* (p. 30). New Orleans: Jupiter: Continental Shelf Associates.
- Paranhos, R., & Ximenez, M. S. (2005). *Programa de avaliação da qualidade da água e efluentes da Plataforma SS-06—Bacia de Campos—Bioincrustação e ictiofauna* (p. 177). Rio de Janeiro: PETROBRAS/BIORIO/IB-UFRJ.
- PETROBRAS [Petróleo Brasileiro S.A.]. (2004a). *Relatório do Programa de Monitoramento Ambiental na Bacia de Campos no Campo de Roncador FPSO Brasil* (p. 124). Rio de Janeiro: Centro de Pesquisas e Desenvolvimento Leopoldo Miguez de Mello, CENPES & Fundação COPPETEC-UFRJ.
- PETROBRAS [Petróleo Brasileiro S.A.]. (2004b). *Monitoramento da Plataforma Continental dos Estados de Sergipe e Alagoas sob Influência de Atividades Petrolíferas* (p. 763). Maceió: PETROBRAS-Petróleo Brasileiro S/A & Universidade Federal de Sergipe.
- PETROBRAS [Petróleo Brasileiro S.A.]. (2006). *Relatório integrador do Programa de Monitoramento Ambiental da Bacia Potiguar* (p. 126). Rio de Janeiro: Centro de Pesquisas e Desenvolvimento Leopoldo Miguez de Mello, CENPES.
- Pozebon, D., Lima, E. C., Maia, S. M., & Fachel, J. M. G. (2005). Heavy metals contribution of non-aqueous fluids used in offshore oil drilling. *Fuel*, 84, 53–61.
- Prego, R., & Cobelo-Garcia, A. (2003). Zinc concentration in the water column influenced by the oil spill in the vicinity of the Prestige shipwreck. *Ciencias Marinas*, 29, 103–108.
- Prego, R., & Cobelo-Garcia, A. (2004). Cadmium, copper and lead contamination of the seawater column influenced by the oil spill on the Prestige shipwreck (NE Atlantic Ocean). *Analytica Chimica Acta*, 524, 23–26.
- Ramos, R., Bastidas, C., & Garcia, E. (2012). Toxicity assays of marine sediments from western Venezuela. *Ciencias Marinas*, 38, 119–127.
- Rezende, C. E., Lacerda, L. D., Ovalle, A. R. C., Souza, C. M. M., Gobo, A. A. R., & Santos, D. O. (2002). The effect of

- an oil drilling operation on the trace metal distribution in bottom sediments from the Brazilian continental platform. *Marine Pollution Bulletin*, 44, 680–684.
- Rezende, C. E., Ovalle, A. R. C., Carvalho, C. E. V., & Lacerda, L. D. (2004). Geochemistry and spatial distribution from two offshore oil fields in Southeastern Brazil. In *Environmental Geochemistry in Tropical and Subtropical Environments* (pp. 355–364). Berlin: Springer.
- Ruus, A., Tollefsen, K. E., Grung, M., Klungsoyr, J., & Hylland, K. (2006). Accumulation of contaminants in pelagic organisms, caged blue mussels, caged cod, and semipermeable membrane devices. In K. Hylland, T. Lang, & A. D. Vethaak (Eds.), *Biological effects of contaminants in marine pelagic ecosystems* (pp. 51–74). Brussels: SETAC Press.
- Salomão, M. S. M. B., Molisani, M. M., Ovalle, A. R. C., Rezende, C. E., Lacerda, L. D., & Carvalho, C. E. V. (2001). Particulate heavy metal transport in the lower Paraíba do Sul River basin, southeastern Brazil. *Hydrological Processes*, 15, 587–593.
- Salomons, W., & Forstner, U. (1984). *Metals in the hydrocycle* (p. 342). Berlin: Springer.
- Silva, C. A. R., Rainbow, P. S., & Smith, B. D. (2003). Biomonitoring of trace metal contamination in mangrove-lined Brazilian coastal systems using oyster *Crassostrea rhizophorae*: comparative study of regions affected by oil, salt pond and shrimp farming activities. *Hydrobiologia*, 501, 199–206.
- Silva, C. A. R., Rainbow, P. S., Smith, B. D., & Santos, Z. (2001). Biomonitoring of trace metal contamination in the Potengi estuary, Natal (Brazil), using the oyster *Crassostrea rhizophorae*, a local food source. *Water Research*, 35, 4072–4078.
- Summerhayes, C. P., Coutinho, P. N., França, A. M. C., & Ellis, J. P. (1975). Salvador to Fortaleza, North-eastern Brazil. *Contributions to Sedimentology*, 4, 44–77.
- Trefry, J. H., Naito, K. L., Trocine, R. P., & Metz, S. (1995). Distribution and bioaccumulation of heavy metals from polluted water discharges to the Gulf of Mexico. *Water Science and Technology*, 32, 31–36.
- Trefry, J. H., Rember, R. D., Trocine, R. P., & Brown, J. S. (2003). Trace metals in sediments near offshore oil exploration and production sites in the Alaskan Arctic. *Environmental Geology*, 45, 149–160.
- Utvik, T. I. R. (1999). Chemical characterization of produced water from four offshore oil production platforms in the North Sea. *Chemosphere*, 39, 2593–2606.
- Vaisman, A. G., Marins, R. V., & Lacerda, L. D. (2005). Characterization of the mangrove oyster *Crassostrea rhizophora*, as a biomonitor for mercury in tropical estuarine systems. *Bulletin of Environmental Contamination and Toxicology*, 73, 582–588.
- Windom, H. L., & Crammer, G. (1998). Lack of observed impacts of gas production of Bangkok Field, Thailand on marine biota. *Marine Pollution Bulletin*, 36, 799–804.