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HEAVY METAL DISTRIBUTION IN SEDIMENTS OF AN OFFSHORE EXPLORATION AREA, SANTOS BASIN, BRAZIL

Giselle da Silveira Abílio[1,*], Ana Cristina Gonçalves Cupelo[2,**], Carlos Eduardo Rezende[3,***]
[1]HABTEC Engenharia Ambiental, ,Av. Treze de Maio, 13 15º andar, Centro, Rio de Janeiro, RJ, CEP 20003-900
[2]ENSR International Brasil, Praia de Botafogo, 440, 24º andar, Botafogo, Rio de Janeiro, RJ CEP. 22250-040
[3]Laboratório de Ciências Ambientais (LCA), Universidade Estadual do Norte Fluminense (UENF)
Av. Alberto Lamego 2000, Campos dos Goytacazes, Rio de Janeiro, 28.013-600
Williams School of Commerce, Economics and Politics, [3]Washington and Lee University
Lexington, VA 24450, EUA
e-mail: *giselle@habtec.com.br, **acupelo@ensr.com, ***crezende@uenf.br

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ABSTRACT

The aim of this study is to consolidate geochemical data obtained from four exploration areas (Santos Basin) before the beginning of the drilling activities. This work was order and coordinate by PETROBRAS. Samples were collected in 30 stations using a Box Core sampler. Metal analyses were performed in bulk sediment samples (0-5cm) and the results pointed that, sorption of metals onto fine sediment particles and onto organic material associated to these particles control the metal distribution. The results suggest that bottom morphology and bottom currents dynamics might be responsible for spatial pattern observed in the area.

RESUMO

Este trabalho objetiva a consolidação dos dados geoquímicos obtidos em 4 blocos exploratórios (Bacia de Santos) antes do início da atividade de perfuração, tendo sido requisitado e coordenado pela PETROBRAS. As amostras foram coletadas em 30 estações utilizando um Box Core. As análises de metal foram feitas no sedimento total (0-5cm) e os resultados mostram que a sorção de metais nas partículas finas do sedimento e na matéria orgânica associada a estas partículas controla a distribuição dos metais. Além disso, a morfologia de fundo e a dinâmica das correntes podem ser responsáveis pelo padrão de distribuição observado na área.

INTRODUCTION

Over the last years, Brazilian government has made several changes related to the exploitation and production of hydrocarbons in the country due to the opening of oil and gas market. In this context, Santos Basin shows up as a promising area that has been the target for many studies aiming at the environmental permits.

Therefore, a good understanding of main impacts of oil and gas industry is needed for a reasonable environmental analysis. Heavy metals are of special concern because they are found as components of most drilling fluids that are commonly discharged in the marine environment (Kennicut II *et al.,* 1996; Conklin *et al.,* 1983; GESAMP 1993; NRC, 2003; Patin 1999; Gray *et al.,* 1999; Breuer *et al.,* 1999).

Therefore, heavy metal concentrations were evaluated before the beginning of drilling activities to establish baseline levels for Santos Basin.

STUDY AREA

The Santos Basin constitutes one of Brazilian coast's largest marginal basement depressions (Pereira e Macedo, 1990), covering São Paulo, Paraná and Santa Catarina States and the southern part of Rio de Janeiro State (Carvalho *et al.*, 1990).

The São Paulo Plateau is located at the eastern part of the Santos Basin, between 2.000 and 2.800m depth (Carvalho *et al.*, 1990; Sombra *et al.*, 1990 e Pereira e Macedo, 1990). Geological studies suggest a continental origin for the São Paulo Plateau basement (Pereira e Macedo, 1990).

This work was demanded and coordinated by PETROBRAS and was carried out by HABTEC Environmental Engineering Company, and comprises the exploratory areas BM-S-8, BM-S-9, BM-S-10, BM-S-11 and BM-S-21 blocks (Figure 1), located at São Paulo Plateau, in the deepest part of Santos Basin.

The oceanic circulation at Santos Basin follows the same pattern of the Brazilian continental shelf (Figure 2). The Tropical Water (TW), formed by intense radiation and

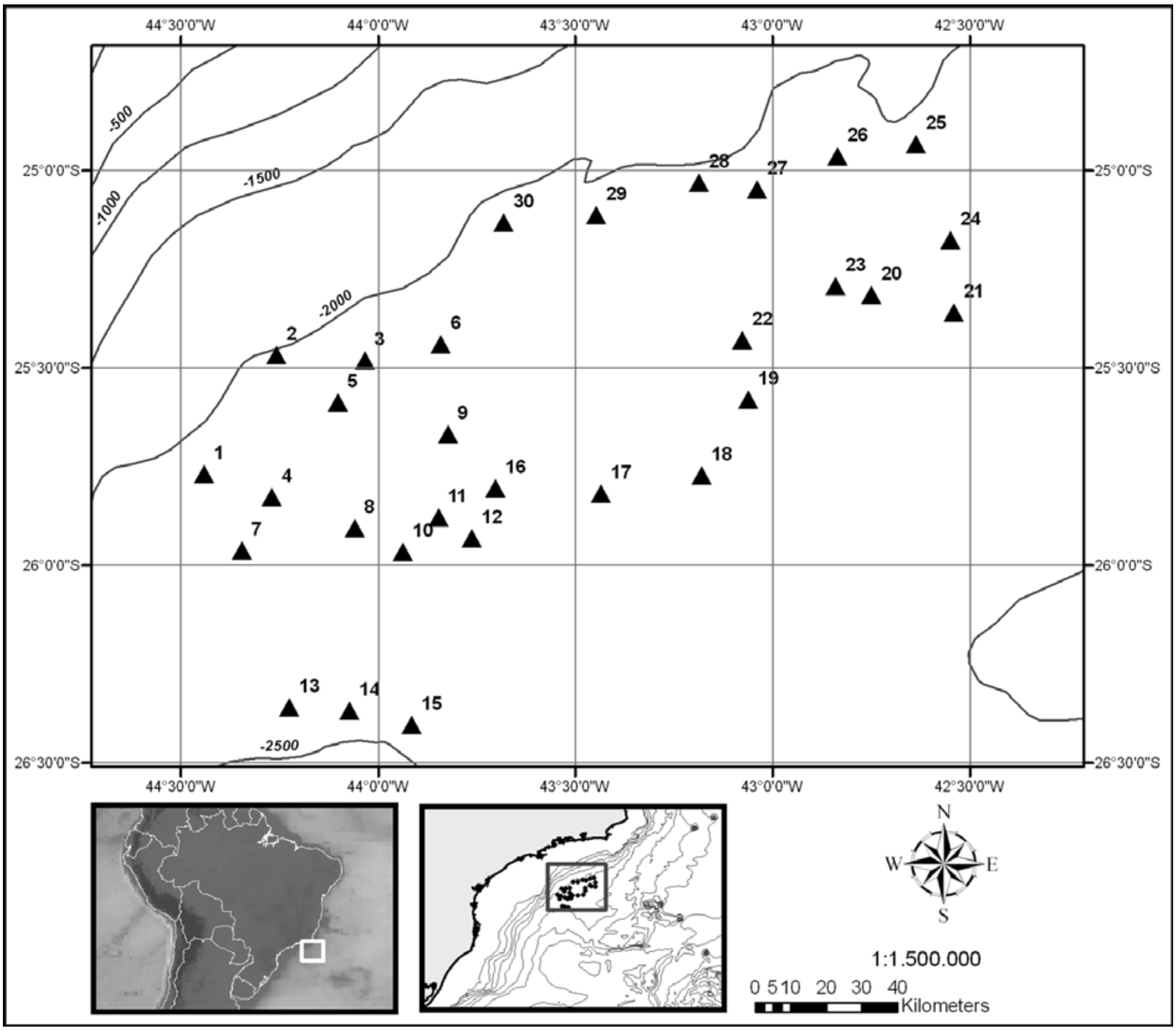

Figure 1: Selected stations in the study area (Santos Basin, Brazil).

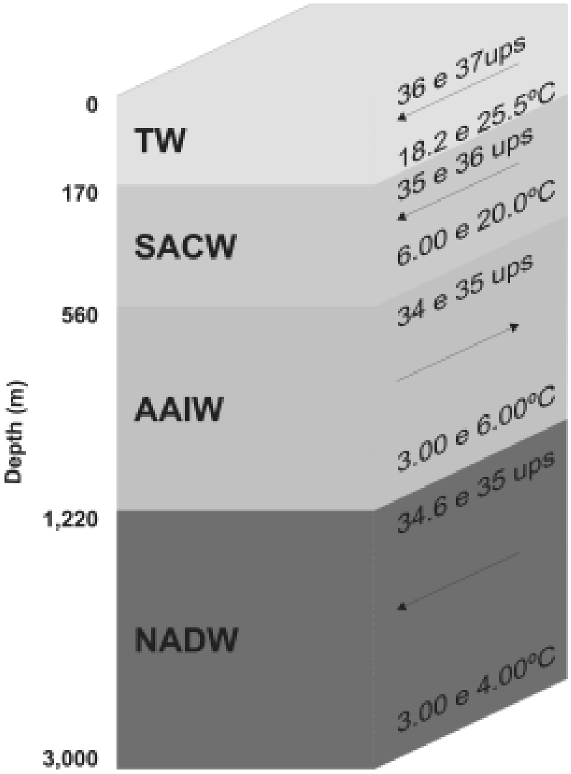

Figure 2: Water masses distribution in Santos Basin (based on Silveira *et al.*, 2000 and Cosendey, 2002).

evaporation (Silveira *et al.,* 2000) is located at the top of the water column, between 0 and 170m depth (Cosendey, 2002). Underlying TW, the South Atlantic Central Water (SACW), spreads between, approximately, 170 and 560m depth. This water mass is limited by salinities ranging from 34.60 to 36.00 and temperatures from 6 to 20ºC (Silveira *et al.,* 2000).

In the Brazilian Continental Shelf, bottom circulation until 3.000m deep is mainly characterized by the presence of the Antarctic Intermediate Water (AAIW) and the North Atlantic Deep Water (NADW). The AAIW has salinities between 34.2 and 34.6 and temperatures from 3 and 6ºC (Sverdrup *et al.,* 1942 *apud* Silveira *et al.,* 2000). The NADW is characterized by salinities from 34.6 to 35.0 and temperatures from 3 e 4ºC (Silveira *et al.,* 2000). According to Stramma e England (1999), the deep range influenced by NADW ranges from 1,200m to 3,900m close to Equator and 1,700m to 3,000m close to the Brasil-Malvinas Confluence Zone. Cosendey (2002) identified NADW between 1,212m and 3,372m with salinities between 34.61 and 34.94 and temperatures from 3.42 to 2.48 ºC.

Simulations with the Princeton Ocean Model (POM) for Santos Basin showed a light SE outflow of the Brazil Current (BC) and a NE counter-flux, as a result of a BC circulation around 27ºS latitude (Chen, 2002). In the northern sector of Santos Basin there is an intense SW outflow close to the shoreline, with a deviation to west close to Cabo Frio. From Cabo Frio, the BC outflow follows far from shoreline, with little deviations, but always following the continental slope (Chen, 2002). The data obtained by Chen (2002) showed that the counter-current is highly represented; flowing to NE, close to continental slope, with velocities up to 0.2m/s. At 1,000m depth, the counter-current is dominant and at Cabo Frio is highly intense.

MATERIAL AND METHODS

Samples from 30 stations (Figure 1) were obtained during an oceanographic cruise in October, 2002. Station locations within the exploratory areas (BM-S-08, BM-S-09, BM-S-10, BM-S-11 e BM-S-21) were defined according to the following criteria: (i) deepest or more eastern isobathymetric contour; (ii) shallowest or western isobath, (iii) intermediated isobath and (iv) bathymetric homogeneity from selected exploratory areas.

Sediment samples were collect with a Box-core sampler. Superficial sediment (0-5cm) was sub-sampled for metal (Cd, Ba, Mn, Zn, Ni, Cu, Cr, Pb and V), organic carbon, carbonate content, and grain-size analysis. Metal analyses were performed by INNOLAB do Brasil LTDA, according to the ISO guidelines (N ISO 11885 E22, N ISO 11885).

Metal Analyses

Heavy metal analyses were performed in bulk sediment samples using an ICP-AES. Dried samples were ground prior to digestion, and 5g sub-samples were separated and digested with 20mL boiling solution $1HCl:3HNO_3$ in reflux during 1h. The extract was obtained by filtration. The quality control was assessed by digestion and analysis of a certified sample. Blanks and a duplicated sample were also processed for each 10 samples. The detection limits obtained were: 5μg/g (Pb); 0,2μg/g (Cd); 3μg/g (Cr, Cu, Ni, Zn, Mn and V) and 1μg/g (Ba). Methodological details, such as recovery factors and calibration procedures, can be found in the ISO guidelines N ISO 11885.

Organic Carbon, Carbonate and Grain Size Analyzes

Organic carbon (OC) content was measured by titration. Samples were digested with $K_2Cr_2O_7$ (0,02N) and H_2SO_4 (50%). Produced CO_2 was fixed with NaOH. Detection limit for OC was 0,005%. Grain size distribution was assessed by sieving and pipetting, for clay fraction, according to Suguio (1973). Statistical parameters (kurtosis, asymmetry, median, mean and standard deviation) were calculated according to Folk and Ward. Carbonate content was assessed by gravimetric method and sediments were treated by HCl (50ºC/~2h; 2g of sediment and 10 mL of HCl 30%).

Baseline Concentration and Ratio-to-Reference Index

As metals occur naturally in the environment, the identification of anomalous concentrations related to sediment contaminations is complicated, especially because direct measures from sediment concentrations do not reflect anthropogenic sources (Schiff e Weisberg, 1999).

One way to identify anthropogenic influences or naturally elevated concentrations is defining a baseline concentration (Singh *et al.*, 2003). The baseline concentration represents a specific concentration in a period of time, that may not reflect true background concentrations (Kabata-Pendias *et al.*, 1992). However, in samples without anthropogenic influences, the baseline concentration can reflect the background levels (Singh *et al.*, 2003). Baseline concentration is normally calculated as the interval that comprises at least 95% from all observations (Kabata-Pendias *et al.*, 1992).

In this work, baseline concentrations calculations were based on the percentile distribution for each metal analyzed. The interval between 5% and 95% of the data distribution was identified with STATISTICA 5.0 ©, and contain almost 90% of the observations. In order to simplify calculations, the median was assumed as the baseline concentration as it is less sensible to minimum and maximum values (Zar, 1996).

The ratio-to-reference (RTR) index was calculated according to Liu *et al.*, (1999). The RTR can be used as a tool to evaluate sediment quality (Liu *et al.*, 1999) or to identify areas with natural enrichment (Moreira e Boaventura, 2003).

Statistical Analyses

In order to separate samples from similar sedimentary composition, cluster analysis (Ward method and Euclidian Distance) was performed. Data from 6 variables (silt content, clay content, carbonate content, total organic carbon and RTR) from all 30 observations, were previously reduced according to eq. 1, where x_i is the variable value, μ is the mean value and sd is the standard deviation for each variable. When statistical analyses based in distance criteria are employed, the data should be reduced to minimize influence values with different orders of magnitude (Howarth e Sinding-Larsen, 1993). Associations between variables were assessed with Spearman (r_s) correlation coefficient (p>0,05).

Figure 3: Distribution of grain-size fractions (a), carbonate content (b) and organic carbon content (c) in sampled stations at Santos Basin.

$$X_i' = \frac{(x_i - \mu)}{sd} \qquad \text{(Eq. 1)}$$

Principal Component Analysis (PCA) was performed with XLSTAT-Pro 7.0©, which uses the r_s to calculate factors variance. Also as done for cluster analysis, variables (clay content, silt content, sand content, carbonate content and metal concentration) utilized in PCA were previously reduced (Eq. 1).

RESULTS

Metal Concentrations

As expected, fine grained fraction (<60µm) content was more than 75% amongst almost all stations (Figure 3a). High sandy content was observed only in samples 2 and 11 (up to 10%).

Carbonate content (Figure 3b) in sediment varied from 48.98% to 65.98%. Mean carbonate content observed was 58.81±4.0% (mean± sd). Spatial distribution of carbonate content in sediments revealed an increasing concentration with depth. High carbonate content suggests an autigenic origin for this material.

Table 1: Reference concentration (median), calculated baseline levels (percentile 5% and 95%) and range (minimum and maximum values).

	MEDIAN	BASELINE	RANGE
		$\mu g.g^{-1}$	
Pb	18.,5	9 – 26	<5 – 28
Cr	31	15 – 37	14 – 37
Cu	20.5	15 – 25	15 – 26
Ni	20	10 – 25	6 – 26
Zn	60	42 – 76	36 – 85
Ba	140	50 – 180	40 – 190
Mn	590	470 – 750	470 – 760
V	41	20 – 52	16 – 54

Organic carbon (OC) content ranged from 0.41% to 0.88%, with mean concentration of 0.71±0.12% (Figure 3c). Distribution of OC in the area showed a low OC level region (stations 1, 2, 7, 10, 11, 12, 14, 15, 16), where OC content is 1.4 times lower than the mean concentration of all other stations.

Metal concentrations (maximum and minimum values) are listed in Table 1. As Cd concentrations were bellow detection limit in all analyzed stations, this metal was not considered in statistical analysis.

In general, spatial distribution of metal concentrations was marked by a higher concentration region at the eastern part of the study area (Figure 4a and 4b). Exceptions are Pb and Mn distribution (Figures 4c and 4d). The spatial distribution of Pb concentrations followed the bathymetric pattern of the area, with higher concentration in the deepest region, while Mn distribution pointed out a lower concentration zone eastward.

Ratio-to-Reference Index

The calculated baseline level for each metal and the median comprises almost the whole data range (Table 2). The median was used as the reference concentration to calculate the Ratio-to-Reference index (RTR).

As can be seen in Figure 5, RTR values were higher (up to 70) in the stations at the eastern part of the study area, when compared to the stations in the western part. Based on RTR index results, the study area could be divided in two different regions: (i) stations from 1 to 16 (western part) with low metal levels and (ii) stations 17 to 30, enriched in metal. This distribution pattern was also obtained in clustering analysis as discussed below.

Table 2:Metal average concentration ($\mu g\ g^{-1}$) at Clusters B1 and B2.

CLUSTER	**A**	**B1**	**B2**
		$(\mu g\ g^{-1})$	
Pb	8.0 ± 9.5	20,1 ± 5.2	7.0 ± 7.2
Cr	17 ± 3.5	34 ± 2.2	22 ± 7.6
Cu	16 ± 1.7	23 ± 1.6	19 ± 0.9
Ni	11 ± 4.4	22 ± 2.2	17 ± 4.2
Zn	44 ± 2.1	68 ± 7.1	51 ± 7.1
Ba	85.0 ± 40.9	160 ± 20.3	75.4 ± 35.5
Mn	490 ± 20.0	606 ± 74.1	636 ± 87.8
V	25 ± 8.2	47 ± 4.8	28 ± 7.8

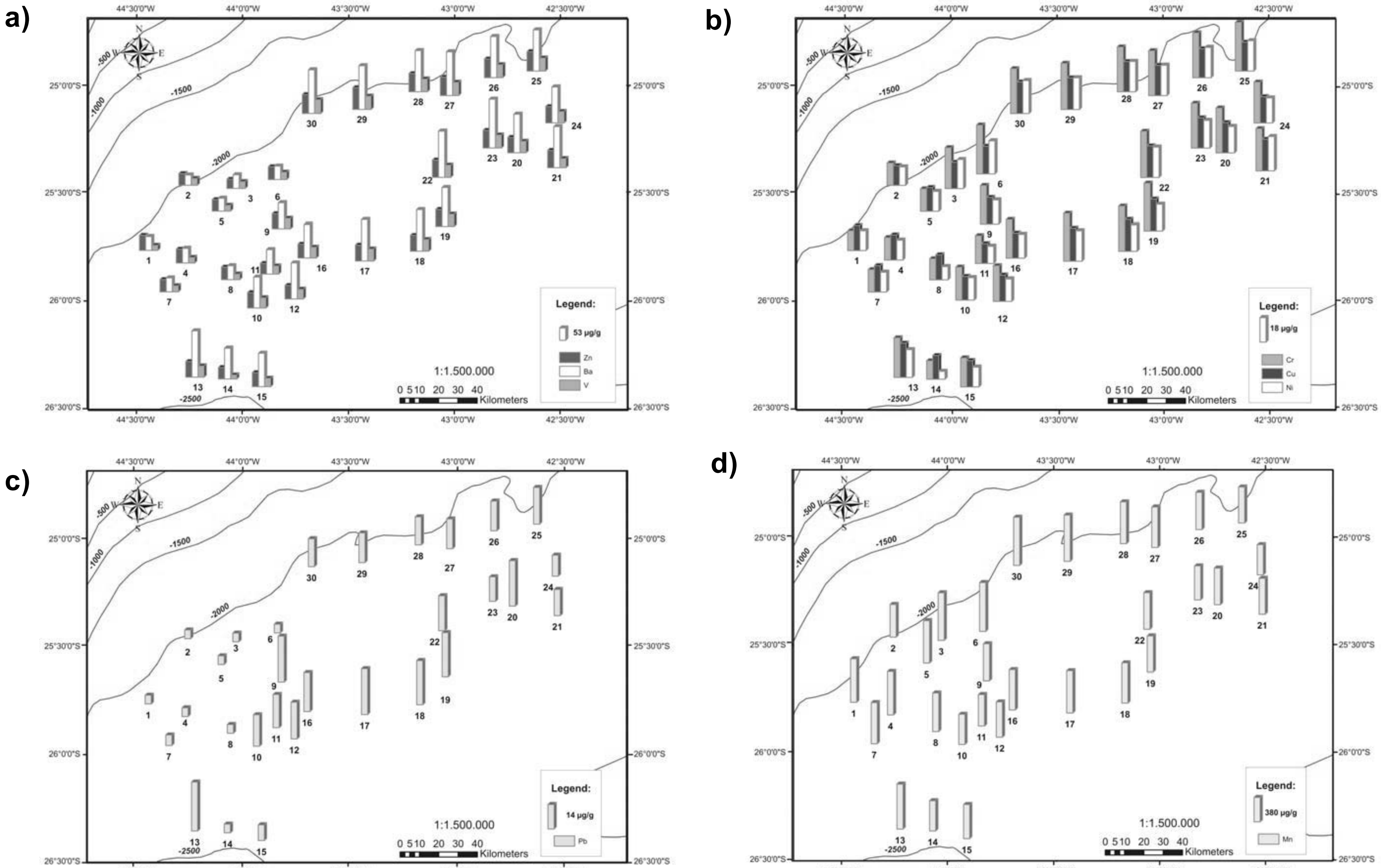

Figure 4: Distribution of metals in sampled stations at Santos Basin: (a) Zn, Ba and V; (b) Cr, Cu and Ni; (c) Pb and (d) Mn.

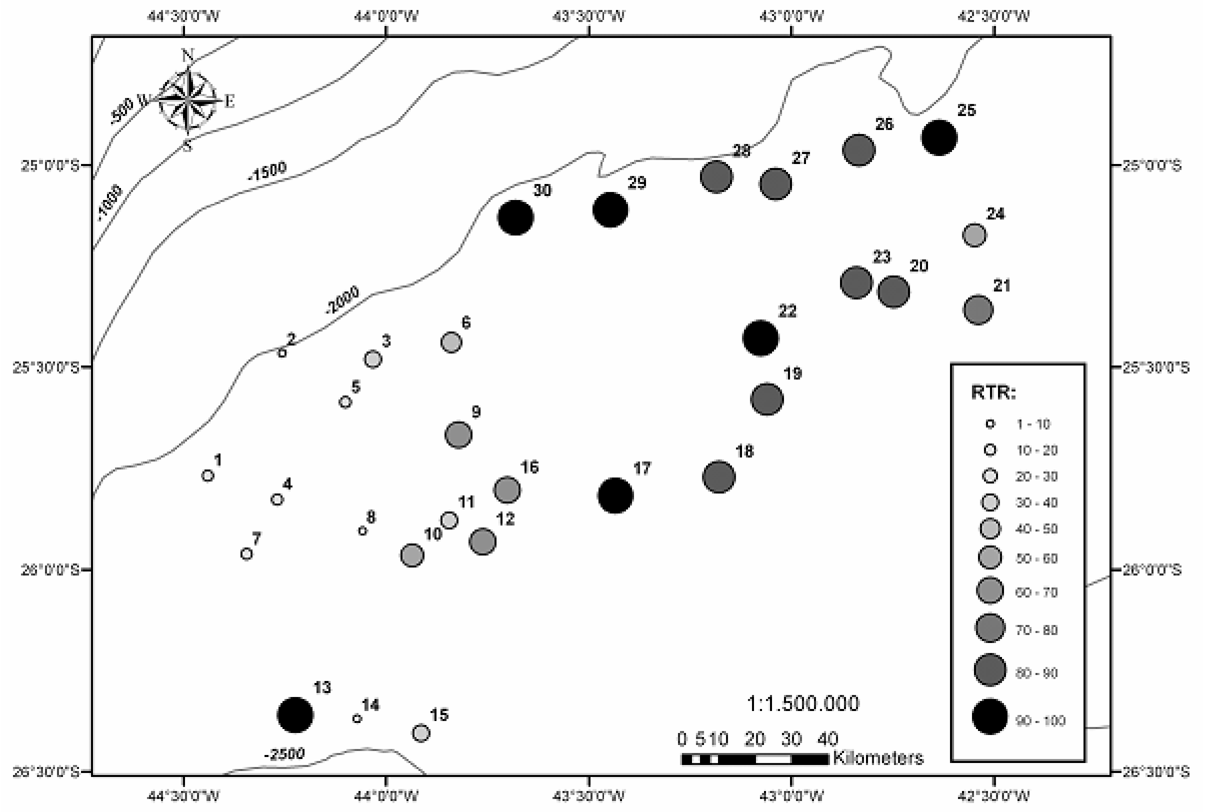

Figure 5: Calculated Ratio-to-Reference index (RTR) in sampled stations at Santos Basin

Statistical Analyses

The cluster analysis pointed out two different groups (Cluster A and Cluster B). Cluster A comprises stations 2, 11 and 14, while Cluster B comprises all other stations (Figure 6). Cluster B was divided in two subgroups (Cluster B1 and B2). Cluster B1 is represented by stations 9, 12, 13, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29 and 30 and B2 group is represented by stations 1, 3, 4, 5, 6, 7, 8, 10, 15 and 16.

Stations at Cluster A might have been separated from Cluster B because of their higher sand content (mean value 10.96%) and very low clay content (minimum at station 14 – 6.54%).

The Cluster B is characterized by high percentage of clay (> 30%), carbonate (> 51%) and organic carbon (> 0.52%). Summarizing, the Cluster B1 has more clay (51.63%) and organic carbon (0.78%) than Cluster B2 (46.91% and 0.68% respectively), with higher average concentration for all metals, except Mn (Table 3).

From all metals analyzed, only Mn did not show negative and significant correlation with sand contents. Positive and significant correlations ($p<0.005$) with clay were observed for all metals except Pb. High correlation obtained (Table 4) seemed to indicate a strong association with clay fraction.

The metals Cr, Cu, Ni, Zn, Ba and V were associated with organic carbon contents. Association between Pb ($rs=0.51$, $p<0.005$) and carbonate could be observed.

Among the analyzed metals, there was a positive and highly significant association between Cr, Cu, Ni, Zn, Ba and V ($p<0.001$). Table 4 shows the selected ($p<0.050$, $p<0.010$ and $p<0.005$) correlations for all variables.

Two factors obtained from Principal Component Analysis explained together 87%

Table 3: Comparison between metal concentrations in different Brazilian environments.

Local	**Depth and Sediment Fraction**	**Pb**	**Cu**	**Cr**	**Ni**	**Zn**	**Ba**	**Mn**	**V**	**Extraction**	
		µg.g^{-1}									
NE sector Guanabara Bay (RJ)	Superficial (<63µm)	69	119			290				HF-(HCl-HNO$_3$) AAS	Faria e Sanchez, 2000
Coastal areas of Rio de Janeiro State	0-2cm (<2,0mm)	15	7.29	24.4	12	32.4	193	168	28.4	HF-HNO$_3$ ICP-AES	Ovalle *et al.*, 2000
São Francisco River (SE-AL)	0 – 2cm (<63µm)		29.0	120	45	190		420		HCl+HNO$_3$ AAS	Carvalho, 1992
Belmonte River (BA)			10.0	43.0	13	77.0		121			
DoceRiver (ES)			19.0	59.0	27	68.0		936			
Paraíba do Sul River (RJ)			29.0	84.0	36	147		876			
Inner Continental Shelf (AP)	n.m.		22.3	74.9	40	128		609		HNO$_3$-HF-HClO$_4$ AAS	Siqueira, 2000
Outer Continetal Shelf (RJ)											
Pargo	0 – 2cm (<2.0mm)	5.5	3.38	15.0	6.2	24.5	165	88.0	15.7	HF-HNO$_3$ ICP-AES	Ovalle *et al.*, 2000
Pampo		6.7	6.30	14.0	7.7	28.9	188	74.8	17.0		
Pargo (beginning of drilling)	0 – 2cm (<2.0mm)	3.8	2.00	11.5	<0.1	8.80	155	78.0	15.6	HF-HNO$_3$ ICP-AES	Rezende *et al.*, 2002
Pargo (7 month after drilling)		3.0	2.60	11.4	2.7	9.70	151	82.0	16.1		
Brazil Basin (NE sector)										HNO$_3$-HF-HClO$_4$ ICP-OES e ICP-MS	Kasten *et al.*, 1998
Sediment	n.m.		29	20	64	38	200	900	50		
Fe/Mn nodules	-		516	62	2304	505	651	158.000	907		
Lower slope /continental rise (Santos Basin)[a]	0 –5cm (<63µm)	18.5	31	20.5	20.0	60.0	140	509	41.0	HCl+HNO$_3$ ICP-AES	This study

Legend: [a]. Median; n.m. not mentioned

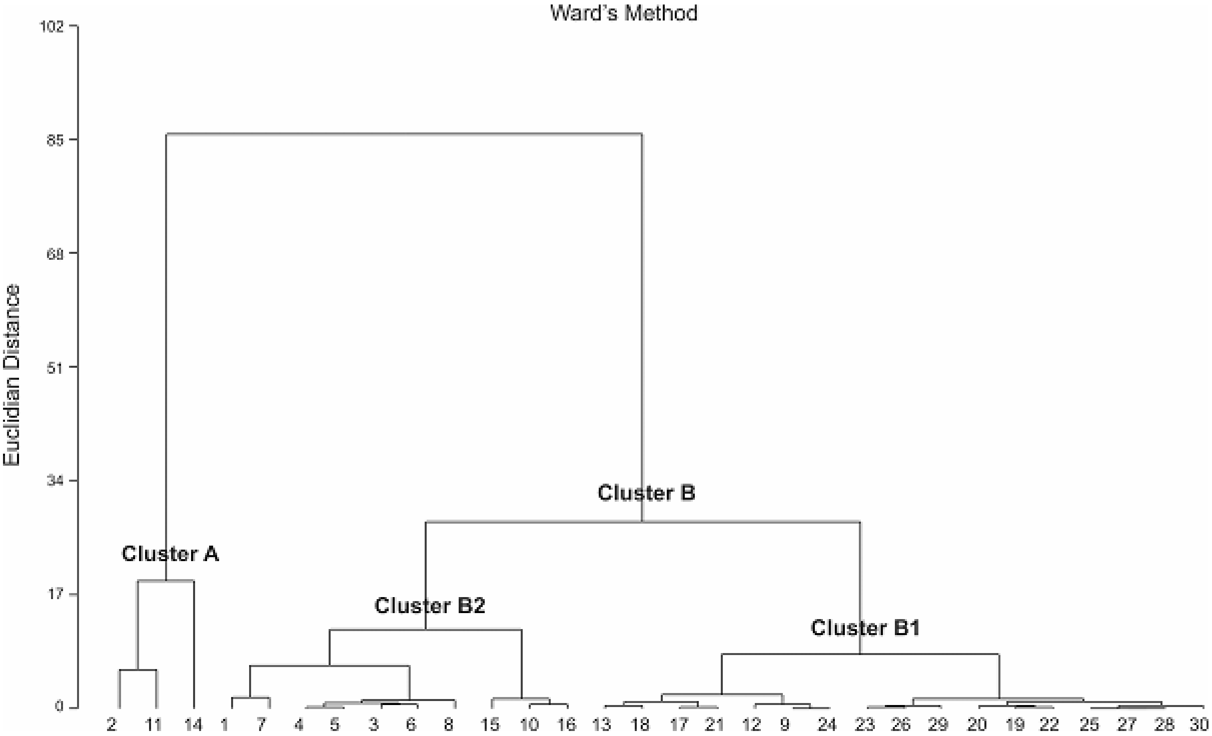

Figure 6: Cluster analysis results.

of data's total variation (Figure 7). Factor 1 (72.4%) separated sand and silt contents from other variables, reflecting a negative association of the coarser grain-size fraction and the metal and organic contents.

Factor 1 also grouped together metals (especially Ni, Cu, Cr, Zn, V and Ba), clay and TOC content, suggesting that these variables could control the metal distribution in the region. Factor 2 was responsible for 14.6% of the data variance. This factor separated Mn (positive portion), Pb and carbonate contents (negative portion), possibly due to low association of these variables and the other variables considered.

Table 4: Spearman correlation coefficient. Stistically significant at the: p < 0,001 (bold), p < 0,005 (Underline), p < 0,010 (Italic) and p < 0,050 (Others).

	Sand	**Silt**	**Clay**	**Carb**	**O.M.**	**Pb**	**Cr**	**Cu**	**Ni**	**Zn**	**Ba**	**Mn**	**V**
Silt	**0.65**	-											
Clay	**-0.74**	*-0.98*	-										
Carb	-0.36			-									
O.M.		-0.43	0.42		-								
Pb	-0.42			*0.51*		-							
Cr	**-0.72**	**-0.57**	**0.63**			0.50	-						
Cu	**-0.78**	**-0.69**	**0.73**	0.39		*0.54*	**0.78**	-					
Ni	**-0.68**	**-0.65**	**0.70**		0.44		**0.86**	**0.80**	-				
Zn	**-0.75**	-0.48	*0.56*			0.42	**0.70**	**0.73**	**0.73**	-			
Ba	**-0.68**	-0.48	*0.54*			**0.58**	**0.63**	**0.81**	**0.64**	**0.84**	-		
Mn		-0.38	0.37						0.42			-	
V	**-0.70**	-0.46	*0.52*			**0.59**	**0.80**	**0.72**	**0.73**	**0.88**	**0.85**		-
TOC	**-0.70**	**-0.69**	**0.71**		0.40		**0.65**	**0.60**	**0.60**	*0.53*	0.49	0.38	**0.60**

Carb = Carbonate; O.M = Organic Matter and TOC = Total Organic Carbon

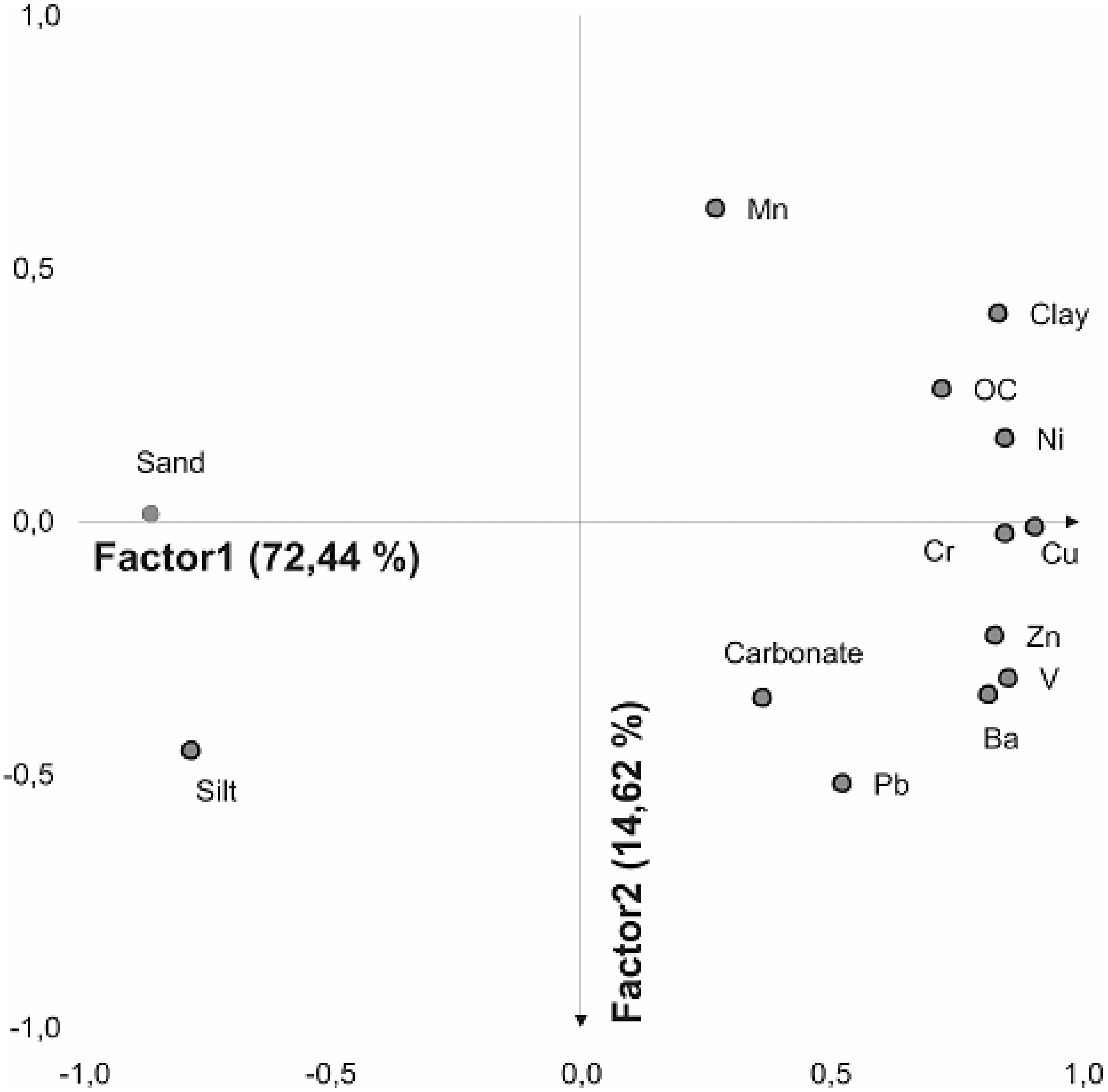

Figure 7: Principal Component analysis.

DISCUSSION

Metal Concentrations

Under a methodological point of view, the HNO_3-HCl extraction, used in this work, is not able to extract the siliceous matrix. In this way, only cations adsorbed to clays, organic matter and oxides are truly analyzed (Cox e Preda, 2003). For refractory elements as Cr, strongly related to siliceous matrix, this extraction is not strong enough, what can lead to underestimated concentrations (Cox e Preda, 2003). The calculated reference concentration of metals found in this study were compared with other studies in Brazil, in different environments (Table 5), as described below.

Lead, Cu and Zn concentrations reported to Guanabara Bay (NE sector) by Faria e Sanches (2001), are higher than the ones found in Santos Basin, as expected. At the Guanabara Bay NE sector, the mangrove organic rich sediment controls the metal distribution (Faria e Sanches, 2001). When compared with concentrations reported by Ovalle et al, (2000) in costal areas of Rio de Janeiro State, similar Pb, Cr and Ba concentrations were found in this study, while Ni, Zn and V were higher in Santos Basin. Concentrations found in Santos Basin for

Cu, Ni, Zn and Mn are similar to those observed by Carvalho (1992) in regions under river influence in the Brazilian Continental Shelf. Only Cr concentrations were lower than the reported by Carvalho (1992). Other study in these regions (Carvalho *et al.*, 1993) pointed out that the transportation of fine grained sediment to deep sea could be responsible for elevated concentrations. In general, concentrations of Cu, Cr, Ni and Zn found in the Continental Shelf near the Amapá State (Siqueira, 2000) are higher than the concentrations observed in the Santos Basin. Mn concentrations at the Amapá Continental Shelf were similar to those found in this study. The metal concentrations observed in Santos Basin are higher than those found in the oil field areas of Pampo and Pargo, both in the Campos Basin (Ovalle *et al.*, 2000; Rezende *et al.*, 2002). Only Cr and Ba concentrations were close to the reported in Pampo and Pargo. The obtained metal concentrations in Santos Basin are similar to those reported for sediment collected in Brazil Basin (NE sector) where metallic (Fe-Mn) nodules are found (Kasten *et al.*, 1998).

Finally, the observed data found in literature for Brazilian regions suggests that metal concentrations found in Santos Basin do not present any anomalous values (Table 5).

Spatial Distribution

Both cluster analyses and RTR index identified zones of varying metal concentrations. In general, the eastern portion presented the higher metal content, what was indicated by elevated RTR values.

In regions such as lower current areas in bottom topographic depressions, the suspended materials might deposit, as observed by Stevenson (2001) in the oceanic region off Scotland.

In the Gulf of Lion slope, in the Mediterranean, off the France cost, lower Mn concentrations were associated with superficial remobilization and mass transportation (Buscail *et al.*, 1997). The Mn distribution appears to be controlled by the bathymetric pattern and the local morphology, with high concentrations in canyon regions (Buscail *et al.*, 1997).

Apparently, the lower concentrations found in the western part of the study area were related to a fast bottom current zone and elevated bottom topography of this region, promoting erosional processes that remove the fine grained and metal rich material. The work developed by Chen (2002) pointed a zone of intense bottom current between 1,000 and 2,000m depth in the western part of Santos Basin.

The inverse process might occur in the eastern zone. At this part, lower bottom currents and a topographic depression could contribute to fine material deposition.

Associations Among the Variables

Hedges *et al.* (1993) showed that a strong correlation between organic carbon and grain-size could be related to carbon adsorbing to the finest fraction, due to the superficial area and same hydrodynamic behavior.

The association of metals and grain-size (positive correlations with silt and clay) shows metal preferential accumulation in finer sediments. This behavior was also observed by Satyanarayana e Ramana (1994), where Cu, Ni, Cr and V concentration showed the same correlation behavior found in this work.

Total organic carbon showed positive and highly significant correlations with almost all analyzed metals.

Only Pb and Cu showed significant and positive correlations with carbonate, being the Pb correlation highly significant. A positive correlation between Pb and carbonates associated with carbonate shells was founded before by Bermejo *et al.*, (2003). Bunett e Patterson (1980 apud Ng e Patterson, 1982) showed that the principal input of soluble Pb to marine biomass in deep sea probably occurs due to the adsorption on surface of primary producers. The atmospheric input can include Pb originated from anthropogenic activities, like industries and automobiles (Ng e Patterson, 1982).

In this work, we observed the presence of a specific metal group, represented by Cr, Cu, Ni, Zn, Ba and V, strongly correlated to each other. Some authors suggest that this association could indicate the same source (Rivaro *et al.*, 1998) or that they are occurring together in lithogenic fraction (Satyanarayana e Ramana, 1994).

Only Mn did not presented strong correlations with other metals, possibly indicating a different source for this metal, as observed by Rivaro et al, (1998). The elevated Mn concentrations in Santos Basin and the absent of correlations with the other parameters could be explained by migration of Mn (Mn^{+II}) toward the sedimentary column and superficial re-precipitation. Lew (1981), observed that in some parts of the Atlantic Ocean, as the region close to the Rio Grande rise, part of the Mn in sediments could be originated by the Mn^{+II} migration from lower layers and by re-precipitation close or at the water-sediment interface.

Li *et al.*, (2000) pointed out the clay fraction and organic matter as mainly controlling factors in metal distribution, with strong positive correlations, indicating the association among metals, clay minerals and the organic contents in sediments.

The PCA gathered a group of metals - Cr, Cu, Ni, Zn, Ba and V close to the vector corresponding to clay content, and also associated with the vector corresponding to organic carbon. These results suggest that this group of metals is possibly controlled primarily by grain-size variation and secondarily by organic carbon, which is adsorbed to the finer fraction.

Through PCA is observed that Pb behaves differently from the other metals. This pattern was also found by Li *et al.*, (2000) in a river in China. The authors also pointed out the atmospheric input as responsible for the distribution of Pb in sediments.

CONCLUSIONS

Comparison between metal distribution patterns and sedimentary parameters found in the study area suggest that bottom morphology and bottom currents controls the sediment distribution, as they are responsible for sediment transportation and circulation. Apparently, processes of metal adsorption onto fine particles and complexation with organic compounds associated to these particles, control metal distribution in the area.

Evidences support the separation of the study area in two different regions: (i) western region (comprising stations 1 to 12), where metal concentrations, clay and TOC contents are lower and the relief is rougher, possibly marked by mass transportation at the slope or erosion by bottom currents; (ii) eastern region, where metal concentrations, clay and TOC contents are higher and the relief is smoother than in the western region. In the eastern region, the smoother topography is possibly facilitating the accumulations of fine-grained sediment, which is organic rich and has a higher metal content.

Some metals (Cr, Cu, Zn, Ba e V) appear to be related to the lithology, probably associated to the dominant clay minerals in the area. However, this could not be confirmed as Fe and Al analyses and clay mineral determinations were not performed in this study.

Concentrations of Pb appear to be related to atmospheric input and/or to accumulation in planktonic carbonatic shells, while Mn distribution might be related to Mn^{+II} migration from lower sedimentary levels, followed by superficial re-precipitation. However, complementary analyses, as sequential extraction, should be performed to evaluate accurately Mn and Pb origins in the region.

Although the concentrations obtained are close to results from other works that even used stronger extractions, further works in the area should give priority to the total extraction and/or to sequential sediment extraction. Analyses of Al and Fe content in sediment should also be included, as they are useful in establishing sediment corrections.

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(Footnotes)

[1] To whom the correspondence should be sent: crezende@uenf.br