Original research paper

SEDIMENTARY TRANSPORT INFLUENCES ON DIAGENETIC PROCESSES AT THE AMAZON CONTINENTAL SHELF, BRAZIL

ABSTRACT

This research aimed to correlate the sedimentary transport with the diagenetic processes in the coastal zone and Amazon Continental Shelf (ACS). Physical and physical-chemical parameters, trace element contents (Cr, Pb, Ni, Zn and Hg), and O_2, CO_2 and iron flux were determined in sediment and pore water. Sedimentary incubation (96 hours) and algorithms were applied to determine the variation of the activity coefficient (ΔI) and ionic strength (F_i) of the predominant chemical species, and to estimate the net production and mineralization of the organic matter (ΔCO_{2T}) in the system. There are not many studies applying incubation tests to identify the diagenetic processes, especially in fluvial-marines sediments. The results showed a strong zonation associated to the transport and deposition processes, influenced mainly by the grain-size and texture of sediment and fluvial streams. The distribution of trace elements followed the trend of the sedimentary pattern, with higher levels of metals in the deposits of clay minerals and organic matter. A factor of weight (F_w), calculated to establish the degree of importance of each parameter under the distribution and mobility of trace elements, suggests that the mobility of Cr, Ni and Zn is controlled by depth, clay and organic compounds contents, and concentration of dissolved oxygen. The vertical flow of O_2 and CO_2 and the Fe^{2+}/Fe^{3+} ratio in the pore water suggest a predominance of organic matter oxidation in the sedimentary layer between 0.0 and 0.2 m, with partially anaerobic mineralization of the sediments below 0.4 m. Increases in trace element concentrations were observed in iron reduction zones, indicating processes of desorption of oxides and hydroxides of Fe and mineralization of organic matter. The extrapolation of the results of the incubation test to the studied system allowed to establish three hypotheses related to the diagenetic processes: 1) the flow of marine currents may be allowing the aerobic oxidation in the sandy sediments, with the nitrification route more accentuated than the ammonification route; 2) in the region of the coastal zone and inner continental shelf the routes of oxidation and reduction may be alternating according to the physical-chemical factors and seasonality; 3) in the coastal zone and inner shelf the net mineralization rate exceeded the net production rate of the organic matter ($\Delta CO_{2T} > 0$).

Keywords: pore water; trace elements; organic matter; mineralization; net productivity; Amazon Continental Shelf.

1. INTRODUCTION

The sedimentary transport regime analysis is much applied in association with geochemistry in quantitative studies, revealing areas of cumulative tendency or sedimentary dispersion. Studies have demonstrated that the sedimentation rate associated with microbiological activity, organic carbon content and seasonal events affect the concentration of dissolved

chemical species directly in the sediments [1,2], especially in water [3,4], which justifies the influence of sedimentary transport on the diagenetic regime, with particular emphasis on quantifying the seasonal rates and spatial patterns of carbon remineralization.

Pore water can be interpreted as a physical-chemical and biological transition phase between what happens in the water and sediment compartments. This suggests a complexity of factors and processes acting jointly in the genesis and flow of chemical species, either by diffusion, advection, precipitation and/or dissolution of minerals, metallic adsorption/desorption, bioturbation, production or mineralization of organic matter [4-6]. The composition (clay and organic matter), physical (porosity) and physical-chemical properties (pH and alkalinity) of the sediments influence in the diffusion and transport of the chemical species in the pore water [5-7], either by vertical or horizontal movements.

In the region between the Amazon and Pará mouths, and the Amazon Continental Shelf (ACS; Fig. 1), the sedimentary dynamics is the largest in the world, both in volume and dispersion area. The distributions of minerals in ACS sediments [8], as well as organic and inorganic components, including trace elements [9], are of unequaled proportions to any other fluvial-marines system on the planet. Fluvial-marines currents play an important role in this sedimentary dynamics, acting individually or together, and seasonally in the Amazonian system. The balance between the erosion, transport and sedimentation processes interferes with the volume of sediments and, consequently, with the concentration of chemical species in the fluvial-marine system. The Amazon River presents the highest suspended solids load transported in the world, about $1.2x10^9$ metric tons/year of sedimentary debris to its lower reaches [10], and that once reaching the continental shelf will submit to a coastal dynamic, mainly by the influence of the North Brazilian Current (NBC) along the American continent. That sedimentary load representing ~3% of the global riverine particle flux, accumulates off the river mouth in Brazilian coastal waters as deltaic mud deposits having a northwest trending strike [11].

Diagenetic reactions and sediment-water exchange processes occurring in deposits of the ACS determining the eventual influence of the Amazon on a range of marine elemental cycles and characteristics of the resulting sediment record [12]. The diagenetic processes involve the genesis of chemical species with consequent alteration in these compositions in the environment. Among the processes involved in diagenesis, the net production and mineralization of organic matter have been highlighted in geochemical studies, as they interfere in the flow and balance of gases (CO_2, O_2, CH_4, H_2S and SO_4^{2-}) in the water and sediment compartments, in the metallic mobilization, and in the aerobic and anaerobic benthic microbial productivity.

This research aimed to correlate the sedimentary transport with the diagenetic processes in the area between the coastal zone and outer shelf of the ACS. For this, 1) the distribution and flow of trace elements (Cr, Pb, Ni, Zn and Hg); 2) the profile of the vertical flow of O_2 and CO_2 in the pore waters, relating them to the iron redox potential (Fe^{2+} and Fe^{3+}); and 3) net production and mineralization of organic matter, identifying the dominant pathway in the pore water system were determined and/or estimated.

2. STUDY AREA

The study has been conducted in the Amazon River, nearby coastal zone (CZ) and Amazon Continental Shelf – ACS (47°52'W-4°19'N and 51°04'W-2°16'S) between Orange Cape (State of Amapá) and Pará River mouth (State of Pará, Fig. 1). It is a dynamic region, influenced by the meeting of continental waters with the Atlantic Ocean on influence at the Equatorial North Current (ENC) and NBC. There is also interference from atmospheric

forces as the Intertropical Convergence Zone (ICZ), generating trade winds and rainfall, which determining the climatic seasons and the hydrological pattern of Amazonian rivers [8]. This complex system of water circulation influences sediment transport and deposition, acting in a selective way to separate the sedimentary fractions and the content of organic material by zonation in the coastal zone and ACS. The climate of the region is "*Am*" hot and constantly humid (monsoon climate) for Marajó Bay, and "*Af*" equatorial for Amazon and Pará mouths, with mean temperature of 28 °C and rainfall exceeding 2000 mm/year, especially between the months of December and February. The Amazon coastal zone includes diverse ecosystems as mangroves, dunes, coastal forests, freshwater coastal, estuaries and river deltas with great aquatic and terrestrial biodiversity associated. Descriptions of the study area and sedimentary patterns can be found in [8,9,11,13].

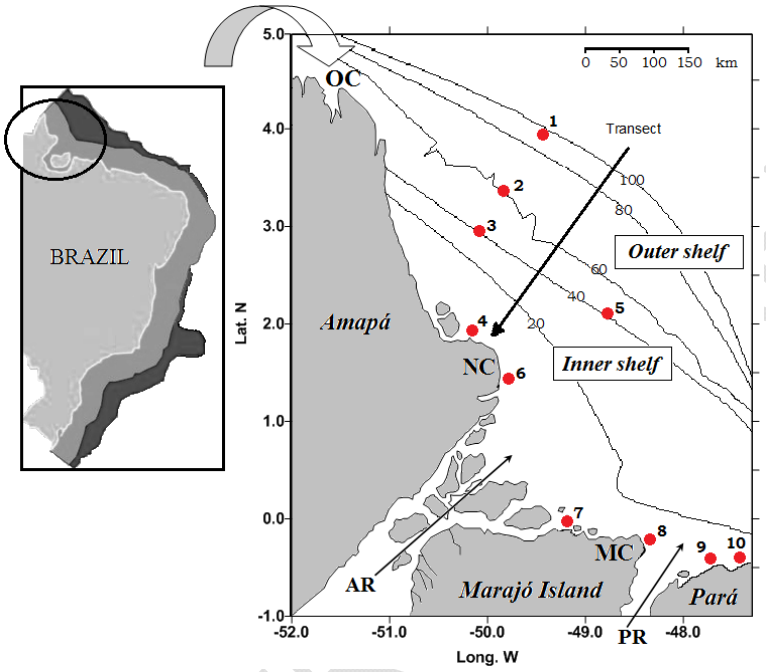

Fig 1. Map of the ACS and coastal zone between Orange Cape (OC) and Pará River mouth. Details of the shelf – coastal zone vector 1 – 4 (transect). Legend: NC= North Cape; MC= Maguari Cape; AR=Amazon River; PR= Pará River; isobaths in meters.

3. MATERIALS AND METHODS

Physical-chemical, water column hydrography and sedimentary load measurements were made following the regime of seasonality in the region. The bathymetric lines (isobaths) showed in the figure 1 were obtained from probe eco-bathymetry and for consultations to nautical charts. A tendency line (exponential fitting curve) with the respective differential equations was determined for the bathymetric profile, with orientation axis from the coastal zone in direction to outer shelf. The sediment samplings, however, were performed during the months of lowest flow (May and June) in the Amazon and Pará rivers and at the ACS. Samples of bottom sediments (0.0 - 0.5 m) were obtained between the 5 and 100 m isobaths using Van-Veen sampler (A=682 cm^2) to the bottom sediments, and box-core sampler (A=177 cm^2) to the vertical samples. The sediment samples were stored in plastic bags and kept in freezer at -5 ºC until the analysis. Vertical samples were used to determine the pH, salinity (u.s.) and dissolved oxygen (DO µmol/L) in the pore water.

At chemistry laboratories at Pará Federal University (UFPA) and National Institute of Research in Amazonian (INPA), the sediment samples used for geochemical analysis were fractionated, oven dried (45±0.5 ºC) and homogenized, sieved and pulverized until very fine sand fraction (125 – 63vfs μm). The pH of the samples was neutralized with 2M NH_4OH solution and 30 mL of Mil-Q water followed by titration of the chloride, to ensure no interference of the Cl- analyzes. For the incubation test, fresh samples were homogenized and stored in polyethylene bottles with a sealed acrylic lid. DO and CO_2 were determined with probes and analytical methods (titration) from the extraction of the pore water, and profiles of oxygen (DO μmol/L) and total CO_2 (ΣCO_2 mmol/L) were established in the vertical layer of the sediments sampled for the vector 1 – 4 (Fig. 1).

Grain-size analysis was determined by the gravimetric method [14]. Organic matter (OM) was determined by hot acidic extraction with excess hydrogen peroxide (30%) at 100 °C [15]. The organic carbon content (OC) was determined by the Walkley-Black method [16], where the organic carbon of the sample is oxidized to CO_2 with potassium dichromate [$K_2Cr_2O_7$] and concentrated sulfuric acid [H_2SO_4]. The chromium of the extractive solution is reduced to Cr^{3+}, and the excess of potassium dichromate is titrated by the ammonium iron (II) sulfate [$(NH_4)_2Fe(SO_4)_2.6H_2O$]. The calculation is done by applying equation 1 [14]. Free CO_2 (CO_{2L} mmol/L) and total CO_2 (CO_{2T} mmol/L) were determinates with probe and also obtained analytically by titrimetric method 4500-CO_2 A and D [17]. The titration was performed potentiometrically with NaOH to bring the sample to pH 8.3 and HCl to pH 4.3. From the results, the carbonate and bicarbonate alkalinities also were calculated. Inorganic carbon (IC) was calculated from the amount of total CO_2 per molar transformation [15].

$$OC = 0.06V(40 - Va \times f) \qquad (eq.1)$$

Where: OC (g/kg); V = volume of potassium dichromate and V_a = volume of ammonium iron(II) sulfate consumed in the reaction; f = 40/ volume of ammonium iron(II) sulfate used in the blank titration; 0.06 = correction factor.

Trace metals Cr, Pb, Ni and Zn (mg/kg) were extracted using mixture [HNO_3 + HCl]:$HClO_4$:HF (Merck 2:1:1) in an open system and determined in a flame atomic absorption spectrometry Shimadzu AA 6800 (Standard Method 3111B modified) [17]. Total Hg (ηg/g) was extracted adding dry sediment and V_2O_5 (1:1) and after a solution of HCl:HNO_3:H_2SO_4 (Merck 3:1:6) in a test tube closed, and determined in cold-vapor atomic absorption (Standard Method 3112B and 3500-HgB adapted) [17]. For analytical quality control, the recovery levels of acid digestion and determination of metals were tested using certified reference material (SRM 2710 near-shore seawater, National Research Council of Canada) analyzed in triplicate. The determinations of the total and reduced iron (Fe^{2+}) fractions were obtained from the methods described by [14,15]. By mass difference the Fe^{3+} fraction was calculated and Fe^{2+}/Fe^{3+} ratio was established. The oxidation potential of the solid-reactive phase of the iron in the sediments was estimated by leaching wet sediment in 6N HCl for 15 minutes at 22°C (10:1 mg sediment/ ml HCl) and analyzing the leachate for total Fe and Fe^{2+}.

The river hydrographic states were used to identify seasonal sampling times, and the respective seasonality. Sampling of the coastal zone and ACS were designed to include a range of major environmental conditions corresponding to changes in likely sedimentation patterns, Amazon River and Para River flows, trade wind stress, and influence of the Equatorial North Current and North Brazil Current (NBC). The study of the diagenetic processes was concentrated at the sampling sites inserted in the vector 1 – 4 (Figure 1), starting at the deepest local (site 1), near the isobath 100 meters, and ending at the coastal zone (site 4), already under influence of the river currents. The sedimentary transport regime

was identified by the analysis of the tendency of space-time clustering of the sedimentary fractions. To estimate diffusive sedimentary flux, the incubation method described by [18] was used. In order to estimate potential diffuse exchange rates and the rates of net production and mineralization of organic matter, samples stored in the sealed vials were shaken vigorously for 5 minutes and then allowed to stand at 20±0.5 ºC and light/dark phases controlled for 4 days (96h). Pore water samples were removed of the sealed vials at incubation times t_0=0h and t_7=96h with a syringe to estimate CO_{2L} and CO_{2T} contents, according to the analytical protocols described by [15,17]. Preliminary tests showed that after four days is more difficult to estimate the diffuse sedimentary flux for the adopted method as well as for the conditions at the ACS, especially in the coastal zone with high OM levels. This occurs because the DO levels after four days are very low almost imperceptible. Thus, a maximum time of measure of four days or 96 hours was established (t_0=0h and t_7=96h in equation 4). Diffusive fluxes of the sediments were calculated from flux (vertical sampling from box core) by dividing the slope of a least squares line fit of the total mass change of a solute at time '*t*' in overlying water versus elapsed incubation time by the area of the flux core. For this study the close system method was adopted for incubation tests (to see item 4.4 Sedimentary incubation). Pore water samples were collected and analyzed for DO and CO_{2T} according to methods already decrypted. The DO and CO_2 curves of consumption/ production in function of the time (Δt) are determined, suggesting the speed of the reaction of the diffuse flux (slow - moderate - fast). Exchange liquid flux by diffusion at the water-sediment interface can be estimated from tables according to temperature and pressure in the environment (pressure of gas diffusion). The net production is obtained from the determination of the CO_2 rates in function of the time (Δt). Using the algorithms of the software Carbmar 1 and 2, and Alcagran (Basic© and TBasic© 1994) and applying equations 2 – 7, the net production rate for $\Delta(CO_{2T})_b < 0 \Leftrightarrow \Delta(O_2)_b > 0$; net mineralization rate for $\Delta(CO_{2T})_b > 0 \Leftrightarrow \Delta(O_2)_b < 0$; and net remineralization reaction rate of the organic matter in the orientation of the vector 1 – 4 (Figure 1) were calculated.

$$I = 0.5 \times \sum\nolimits_i Z_i^2 [i] \qquad (eq.2)$$

$$Logf_i = -A \times Z_i^2 \times \left[\left(\frac{I^{1/2}}{1 + I^{1/2}} \right) - 0.3I \right] \qquad (eq.3)$$

$$\Delta(CO_{2T})_a = 0.5 \times (FCO_{2T}(t_0) + FCO_{2T}(t_7)) \qquad (eq.4)$$

$$\Delta(CO_{2T})_b = \Delta(CO_{2T}) - \Delta(CO_{2T})_a \qquad (eq.5)$$

$$C_{eq} = C + \frac{Mn}{6} + \frac{(Cr + Mo + V)}{5} + \frac{(Ni + Cu)}{15} \qquad (eq.6)$$

$$\sum \Delta M(t) = [C(t) - Cc(t - \Delta t)] \times V' \qquad (eq.7)$$

Where: [eq.2] I= is the activity coefficient of the ionic functions; i = major ionic species with corresponding electrical charges (Z); [eq.3] f = ionic strength for A= 0.5 [19,20]; [eq.4] $(CO_{2T})_a$= exchange liquid flux by diffusion at the water-sediment interface in the interval *t*, and FCO_{2T} in t_0 and t_7 represent the flux of CO_2 in each moment *t*; [eq.5] $(CO_{2T})_b$= net production or mineralization rate of CO_{2T}; [eq.6] C_{eq}= represents the equivalent carbon with the element contents in %; [eq.7] C(t) = solute concentration at time t; Cc = concentration of solute corrected in the previous sample as a function of time variation (*t* - Δ*t*) ; and V = volume of water overlying the core [18].

4. RESULTS AND DISCUSSION

4.1. Sedimentary characterization

Table 1 presents some relevant characteristics of the sediment and pore water determined at the ACS. The granulometric analysis revealed the presence of mud sediments with high percentage of fine silt and clay in the coastal zone, with variation of 80.6 – 90.6% (mean 84.8±3.6%). In the continental shelf area, not making a distinction between the influence of the river and marine currents, the values had high variation, from 5.8 to 81.4% (mean 53.6±29.1%). Isolating the areas by influence of the currents, we have that the ACS inner shelf (sites 3 and 5) had concentrations of fine sediments between 70.7 – 81.4% (average 76.0±5.3%); and on the outer shelf (sites 1 and 2) from 5.8 to 56.1% (mean 31.2±25.5%). The coastal zone and the inner shelf presented enrichment of the bottom sediments with fine organic material originating from Amazon River sedimentary load. A similar pattern of change in particle size was observed by [13,21], along the Amazon Shelf between 10 and 50 meter isobars above the North Cape (State of Amapá). According to the authors, the transition in the sedimentary pattern extended from the interior delta of the Amazon River towards the inner shelf with extensively reworked by intense tidal currents and waves. The bathymetry suggests a behavior in a little negative exponential curve. In other words, the increase in the depth of the coastal zone towards the ocean floor was slightly mild, with two very evident areas of reduction in the inclination of the curve: first one at 40 meters and the second one near 80 meters deep (Figure 2A). The trend of accumulation of fine sediments in the fluvial-marine environment followed a distribution pattern, which can be explained by a variation of the Gaussian curve. The sedimentation – deposition and physical-reworking patterns indicated an area of maximum thickness of the thin sediment layer with approximately 62 cm high and 49 km away from the coastal zone (Figure 2A). Similar patterns were observed by [11,12]. Aller et al. [12] observed a layer of fine sediment between 50 and 60 cm thick accumulated about 65 km from the coastline, above the North Cape between 1.5º and 3.5º north latitude, which the authors identified as a result of physical reworking of sediments from a circulation pattern influenced by NBC. According to the authors, vertical sediment-water zonation in particle mobility and concentration are therefore typically present at the region, with the relative zonal thicknesses determined seasonally by the relative dominance of physical processes and sediment supply at each site.

The organic matter (OM) and organic carbon (OC) contents in the study area varied, respectively: in ACS (sites 1, 2, 3 and 5) OM= 0.6 – 2.8% (mean 1.3±0.4%) and OC= 0.3 – 1.8% (mean 0.8±0.3%); only on the outside of the shelf, under the influence of marine currents, OM= 0.6 – 2.8% (mean 1.5±0.5%) and OC= 0.3 – 1.8% (mean 0.8±0.3%); in the inner shelf, OM= 1.0 - 1.6% (mean 1.2±0.2%) and OC= 0.6 – 0.9% (mean 0.7±0.1%). As expected, the coastal zone presented the highest individual OM and OC contents in the sediments, varying between OM= 2.2 – 4.9% (mean 3.3±0.7%) and OC= 0.5 – 2.7% (mean 1.5±0.7%). Most OM in water and sediment occurs as OC that has functional groups that form stable complexes with trace metals, due to its capacity of cations adsorption. Thus the presence of OC tends to increase the dissolved fraction of metals [22]. The decomposition of OM can affect both hydrodynamic processes and geochemical redox cycles, providing driving forces for metal mobilization [23]. The mobilization and distribution of trace metals in water-sediment systems are dependent on physical-chemical, especially pH and redox changes (DO levels), and microbiological mechanisms, mediated by the species transformation [24,25], as is observed in the diagenetic processes. The physical-chemical mechanisms involved include metal speciation, adsorption, precipitation, co-precipitation and diffusion [22,26]. The capacity of sediments to adsorb and retain trace metals is also dependent of other variables as the availability of Fe and Mn, presence of carbonate and the clay minerals levels.

The accumulation of OM associated to fine fractions of clay increased the porosity of the sediments at the coastal zone (0.66 – 0.7 ml/cm^3), while in the outer shelf, owed mainly the

uniformity of the grain size, the sandy sediments presented the smallest porosities values (0.28 – 0.34 ml/cm^3, Table 1). The porosity is defined as the amount of water that a rock or sediment can store. For this reason, porosity also can interfere in the metallic ions levels and consequent mobilization and distribution in the pore water, allowing the accumulation (stock) of metals in the sediment compartment.

The SiO_2/Al_2O_3 ratio followed the same trend presented for grain size, with a total variation in the study area from 3.7 (site 4) to 30.3 (site 1), and averages by zoning of 13.3±10.8 in ACS; 4.3±0.5 in the inner shelf; 22.3±8.1 in outer shelf; and 6.7±1.3 in the coastal zone. These results confirm the proportion of silicates as a function of sediment transported, with a strong distinction between the low SiO_2/Al_2O_3 ratio in the sediments deposited by the fluvial currents (Amazonas and Pará rivers) and the high ratio in the sandy sediments reworked by the marines currents (Figure 2B). It is correct to say that the sediment characteristics found at each sampling site were influenced not only by the currents, but also by the depth of the bed. The shallower areas presented higher sedimentary deposition load, with accumulation of fine sediments. On the other hand, the deeper areas presented greater resuspension and swirling capacity, preventing the deposition of fine sediments.

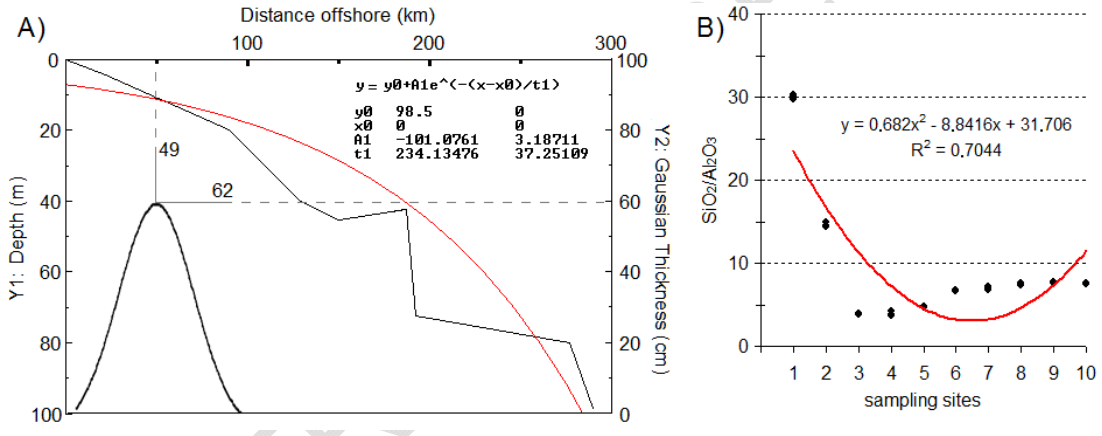

Fig. 2. A) Graphic representation of the oceanic relief (bathymetric profile) with exponential fitting curve (red line) and respective differential equations, behavior of sedimentation – deposition processes and physical-reworking patterns in the coastal zone and ACS; B) Distribution pattern of the SiO_2/Al_2O_3 ratio in the coastal zone and continental shelf with respective parabolic fitting curve (red line of tendency) and equation.

Table 1. Some characteristics of the sediment and pore water determined at the ACS (minimum and maximum values by zone).

	Sediment					Pore water				
	Water depth	Porosity	Sand	Silt+Clay	OC	Salinity	pH	O_2	Fe^{2+}	Fe^{3+}
	m	ml/cm^3	%	%	%	u.s.		%	mmol/L	mmol/L
ACS*	40.0	0.25	18.6	5.8	0.32	35.5	7.99	22.79	0.02	0.04
	98.5	0.40	94.2	81.4	1.78	38.4	8.21	57.60	0.03	0.05

CZ	4.5	0.66	9.4	80.6	0.46	4.9	6.51	5.64	0.04	0.04
	8.3	0.70	19.4	90.6	2.70	6.0	7.84	18.63	0.06	0.07
Inner	40.0	0.25	18.6	70.7	0.55	35.5	7.99	22.79	0.03	0.04
	42.2	0.40	29.3	81.4	0.88	37.7	8.21	38.54	0.03	0.05
Outer	72.4	0.28	43.9	5.8	0.32	36.3	8.03	39.37	0.02	0.04
	98.5	0.34	94.2	56.1	1.78	38.4	8.18	57.60	0.02	0.05

*ACS= sites 1 to 3 plus 5; CZ= sites 4 plus from 6 to 10; Inner= 3 and 5; Outer= 1 and 2.

4.2. Distribution of trace elements

The trace metal contents varied between Cr 36.5 – 86.4 (71.0±13.2); Pb 54.2 – 108.0 (85.9±17.3); Ni 15.8 – 34.0 (25.1±6.1); and Zn 76.0 – 135.0 (108.0±21.7) mg/kg and Hg 66.0 – 113.2 (77.8±11.4) ηg/g (Figure 3A). The following behaviors were observed: 1) tendency to greater fraction of fine sediments in the inner shelf by direct influence of the high sedimentary load of the Amazon River mouth; 2) absence of OM in the sediments of the outer shelf by the continuous flow of the ocean currents from southeast to northwest; 3) a strong seasonality in the volume of sediment transported due to rainfall. The concentration of trace metals in the sediments followed the same convergence observed for the sediment flow, establishing a pattern with higher levels of trace metals in the CZ and inner shelf, and lower levels in the outer shelf (Figure 3B).

An important aspect in the flow of metals is the high capacity of metallic adsorption by the clay minerals in the sedimentary transport regime (discussed in the item 4.1). The high cation exchange capacity observed in the clay and OM particles, associated to the slightly acidic pH conditions in the fluvial-marine system, contributed to the storage of the trace metals especially in the inner shelf, as bivalent forms. This explains the positive correlation pattern calculated for OM, clay and trace elements. The Pearson correlation indexes calculated between OM and trace elements ranged from 0.516 Hg to 0.783 Ni (Table 2). There was also observed a significant correlation between OM and fine clay particles (0.776). In relation to the adsorption and desorption processes of the particles, the increase of the silicate load in the sediments of the outer shelf reduced the OM and clay contents and, consequently, of trace elements available for mobilization. The bioavailability of a trace metal, and consequently its toxicity, both depend on the form in which the metal is found (degree of speciation). Factors such as pH, Eh, alkalinity, degree of oxidation, suspended solids (OM and clay minerals), oxygen and temperature interfere with the mobility/precipitation ratio of trace metals. The pH has an important controlling role in the precipitation of the metallic elements through its ability to attack the minerals of rocks, soils and sediments [22], inducing the leaching or solubilization of the metals. During the leaching process, oxygen can be partially consumed to oxidize OM and reducing it to simpler inorganic fractions. Thus, the contribution of O_2 transferred from the cooler ocean currents to the sedimentary layer, especially in the first half meter, interferes in the OM-metals and clay-metals adsorption mechanism, a tendency observed in the negative correlation between the parameters. The depth of the sedimentary bed also showed a significant correlation, in this case with OM, sedimentary fractions, pH and salinity (Table 2).

A normalization index was applied to the absolute values in order to establish the importance or 'weight factor' (F_w) of each parameter under the distribution and mobility of trace elements in the studied area. The normalization to establish a 'weight factor' is a practice usual in the creation of indexes such as the Water Quality Index, first applied by [27] for the National Sanitation Foundation (US NSF). Equation 8 presents the applied normalization calculation. The numerical values in front of each parameter indicate their 'weight' of importance in the general tendency, and the signal (positive or negative) of each parameter indicates if the proportionality was direct or indirect in relation to the concentration

of trace elements in the sediments. The results suggest that the mobility of Cr, Ni and Zn is strongly related to the depth and location of sampling sites; sand, clay, OM and OC levels, and the DO concentration (Table 3).

$$Fw = \frac{Avr \times (SD)^2}{Max^2 - Min^2} \qquad (eq.8)$$

Were: F_w= weight factor; Avr= average; SD= standard deviation; Max= maximum and Min=minimum.

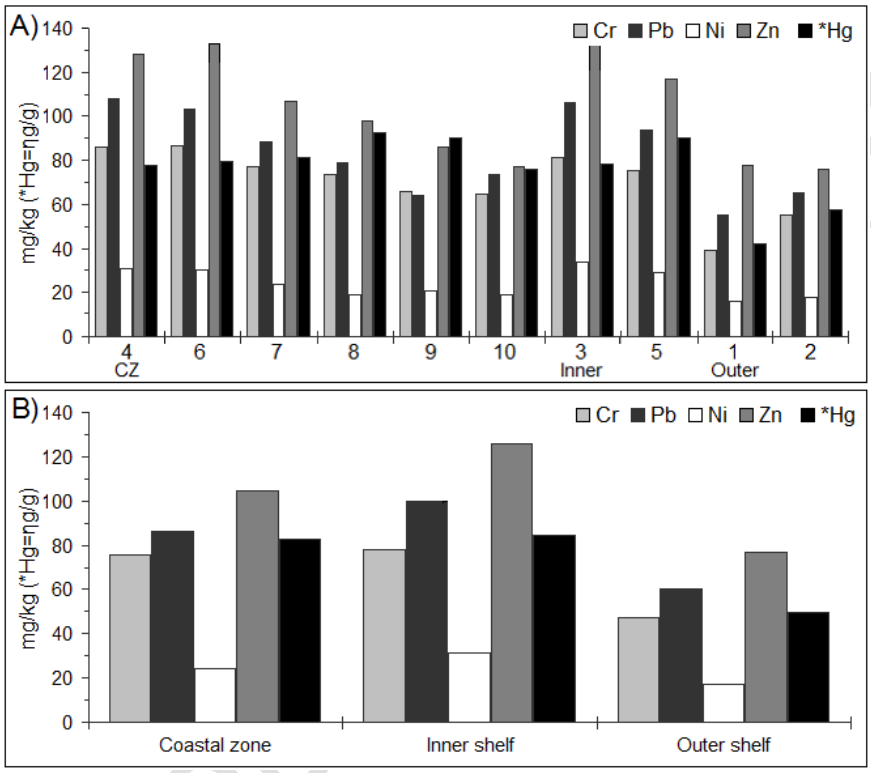

Fig. 3. Medium concentration and trend of the trace metals in the CZ and ACS, Blue Amazon – Brazil.

4.3. Diagenetic processes

The series of physical-chemical transformations of OM, occurring in the water and sediment compartments, including pore water, is known as diagenesis. It is an essential process for the cycling of nutrients, allowing the renewal of marine life. In the diagenesis, several redox reactions occur due to the decomposition of OM by bacterial activity (reactions of Froelich et al. [28], whose main regulating factor is the concentration of DO in the sedimentary layer, especially in pore water. In aquatic sediments it is usual to continuously produce organic compounds through decomposition, by aerobic and anaerobic pathways, as well as mineralization of OM from the breathing and fermentation processes. Add to this autochthonous organic load the volume of organic compounds carried by the streams,

especially bottom streams, and deposited over an area, incorporating organics compounds into the processes mentioned above.

Table 2. Pearson's Correlations: bold correlations are significant at $p< 0.050$ and $n= 110$ (values with 3 decimals ±.xyz).

	Depth	OM	OC	IC	Sand	Silt	Clay	Si/Al	DO	O_2%	pH	Sal	Cr	Pb	Ni	Zn
Depth	1.0															
OM	**-.703**	1.0														
OC	-.476	**.875**	1.0													
IC	.424	**-.718**	**-.860**	1.0												
Sand	**.915**	**-.715**	-.556	.343	1.0											
Silt	**-.737**	.383	.205	-.202	**-.912**	1.0										
Clay	**-.944**	**.776**	.537	-.386	**-.958**	**.760**	1.0									
Si/Al[1]	**.803**	**-.780**	**-.692**	.085	**.937**	**-.863**	**-.892**	1.0								
DO	-.464	**-.719**	**-.677**	**-.704**	-.145	.082	.233	.105	1.0							
O_2%	-.299	**-.644**	-.525	-.312	.011	-.125	.081	.249	**.948**	1.0						
pH	**.686**	**-.713**	**-.754**	**.711**	.565	-.429	-.599	.293	-.531	-.419	1.0					
Sal[2]	**.882**	**-.830**	-.583	.522	**.849**	-.466	**-.709**	.444	**-.801**	**-.662**	**0.755**	1.0				
Cr	-.565	**.632**	**.601**	-.226	**-.715**	**.738**	**.729**	**-.840**	-.408	-.307	.070	-.476	1.0			
Pb	-.258	**.617**	.540	-.507	-.425	.490	.437	**-.650**	-.592	-.444	.418	-.229	**.909**	1.0		
Ni	-.034	**.783**	**.666**	**-.612**	**-.674**	.529	.340	-.522	**-.758**	-.473	.573	-.474	**.794**	**.926**	1.0	
Zn	-.041	**.732**	**.663**	**-.611**	-.231	**.634**	.337	-.470	**-.650**	-.564	.586	-.409	**.821**	**.945**	**.961**	1.0
Hg	-.515	.516	.497	.013	**-.691**	**.809**	**.624**	**-.714**	-.324	-.251	.070	-.489	**.789**	**.705**	**.627**	.573

[1] SiO_2/Al_2O_3; [2] Salinity.

Table 3. Weight factor (F_w) of the parameters analyzed in the distribution and mobility of trace elements.

depth	OM	OC	IC	sand	silt	clay	Si/Al	DO	O_2%	pH	sal	Cr	Pb	Ni	Zn	Hg
-0.9	**0.9**	**0.8**	-0.6	**-1.0**	0.6	**0.8**	**-1.0**	**-0.8**	-0.6	0.1	-0.3	**0.8**	0.6	**0.8**	**0.7**	0.6

*Bold= values with significance at $p< 0.050$.

The relationship between the production and consumption of organic material defines the metabolism of an ecosystem, in this case benthic or sedimentary. In the euphotic zone, the processes of production exceed the mineralization in the diurnal phase [$\Delta(CO_{2T})_b$= -n], reversing the direction of the reaction at night [$\Delta(CO_{2T})_b$= +n]. In addition to O_2, physical and physical-chemical factors such as stream flow, sediment porosity, sedimentation rate, water-sediment interface temperature, pH, alkalinity, cation exchange capacity (CEC), trace element concentration, OM, respiration rate and intensity of benthic biological activity determine the way diagenesis occurs, especially in the time of nutrient regeneration rate. By analyzing the sampling sites by zoning, it was possible to identify areas of low O_2 content, with an increase in CO_{2T} levels. These results suggest moments of reduction of Fe^{3+} and Mn^{4+} (equations 9 and 10) [28], especially in areas with high OM content and protected from currents such as site 4 below 0.2 meters (Figure 1). Degradation of the organic matter by the reduction of Mn^{4+} (eq.9) is thermodynamically more favorable than the reduction of Fe^{3+} (eq.10). However, the iron reduction pathway is considered to be more important for the mobility and/or co-precipitation of trace elements in the coastal zone and inner shelf, because the total Fe concentration in the Amazonian continental waters is about 100 times higher than the concentration of manganese. The mean total Fe and Mn concentration determined in the Amazon River waters is 1.3 – 3.4 mgFe/L and 0.009 – 0.08 mgMn/L (Darwich and Aprile, unpublished data). Sequence of oxidant species observed in the sedimentary layer [28]:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 236MnO_2 + 472H^+ \rightarrow 236Mn^{2+} + 106CO_2 + 8N_2 + H_3PO_4 + 366H_2O \quad \text{(eq. 9)}$$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 212Fe(OH)_3 + 636H^+ \rightarrow 212Fe^{2+} + 106CO_2 + 16NH_3 + H_3PO_4 + 636H_2O \quad \text{(eq. 10)}$$

Although in the coastal zone and inner shelf areas occurs large deposition of OM, factors such as slightly alkaline pH and low interstitial O_2 levels may be contributing to the reduction of mobility of trace elements. Considering that part of the DO content is being consumed by the OM oxidation, the process of deposition and reduction of the metallic mobility intensifies, ensuring that this sedimentary layer acts preferentially as a storage compartment (stock) of trace elements. Vertical profiles of the O_2 and ΣCO_2 contents in the pore water of the sedimentary layer of the sampled sites were elaborated (Figure 4). In general, the sandy sedimentary layer had a greater flow of oxygenation than the mud layers of the coastal zone and inner shelf. DO contents in the 0.0 – 0.5 m ranged from 95.6 – 178.1 µmol/L on the outer shelf; of 66.5 – 112.5 µmol/L on the inner shelf; and 3.1 – 54.4 µmol/L in the coastal zone (Figure 4). The bottom currents in the outer shelf, cooler and oxygenated, they interfered in the sedimentary O_2 flux, facilitated by the porosity of the sandy sediments. It can be pointed out that the diffuse oxygen flux in the sediments was directed by the consumption in the oxidation process. The oxidation of organic matter in fluvial-marines sediments is considered the most important form of respiration in fluvial-marine sediments [29]. Besides, another factor may be contributing to diffuse oxygen flow, in this case a biological action involving benthic respiration, especially in coastal sediments. Studies on oxygen flow and oxireduction of nitrogenous and sulfated forms (NO_3 and SO_4) performed in the same region demonstrated the importance of the benthic respiration in diagenetic processes [29-31]. In general, aerobic respiration takes place in the oxic surface layer and is followed by nitrate and sulfate reductions. However, in coastal sediments the oxic zone often is only a few millimeters thick, as suggest the studies of [12] and [28], and exactly as observed in the sediments of the coastal zone and inner shelf of the ACS, where the anaerobic respiration becomes dominant. Besides, much of the oxygen uptake is used to reoxidate the products of anaerobic respiration as H_2S, NH_4^+ and CH_4 at the oxic/anoxic interface of the sediment [32].

The mineralization of the anaerobic organic matter involves several oxidation processes, consuming nitrates, Fe and Mn oxides, sulfates and carbonic acid to form CO_2 and fermentation, in this case with formation of CH_4 (methanogenesis). Due to its greater stability in relation to H_2S and SO_4^{2-}, the CO_2 becomes an important indicator of diagenetic processes. In general, is considerate for analysis the sum of all dissolved carbonate forms, which are defined as total inorganic carbon or CO_{2T}. The concentration oscillation of both free CO_2 and CO_{2T} depends directly on the production and consumption in the processes already mentioned, pH, alkalinity of the carbonates and ionic composition of the water. The carbonate content, which interferes with pH and alkalinity, has as main source in the marine environments the contribution carried by the waterways and biogenic production, whose main raw materials are plankton and mollusks. In relation to carbonate content, in the Amazonian plain the main source of carbonate is predominantly HCO_3^- [33]. The biogenic production of carbonate in shallow waters and its dissolution in deep waters causes a dynamic equilibrium system, affected by ocean currents, and that controls, among other factors, the concentration of total inorganic carbon in the system. The CO_{2T} contents presented some variability as a function of zonation, ranging from 3.3 – 4.3 mmol/L in the outer shelf; of 3.3 – 4.7 mmol/L on the inner shelf; and 3.2 – 7.8 mmol/L in coastal zone sediments (Figure 4). The higher CO_2 levels in the sediments are associated with decomposition processes and complete oxidation of organic matter and mineralization partially anaerobic of the sedimentary particles. All the sampling sites showed a considerable capacity for a rapid change in pore water constituents associated with the remineralization processes, suggesting the presence of abundant organic compounds, especially in the inner shelf that, as mentioned above, act primarily as a storage

compartment of thin sediments, depending on their morphology and flow direction. At some sampling sites, the exponential decay of O_2 occurred simultaneously to CO_2 production, especially at depths of 0.0 – 0.2 meters in the sedimentary layer. This behavior reflects the nature of particle deposition and reworking of particles. It should be remembered that the samplings and measurements were carried out during the months of the lowest flow in the Amazon and Pará rivers and at the ACS. Thus, it is plausible to believe that seasonality can alter the flow pattern of oxygen as well as CO_2 during the hydrological year, especially during the periods of higher flow of the Amazon River, when the sediment load transported can reach double volume, as has been suggested by [10] and [13].

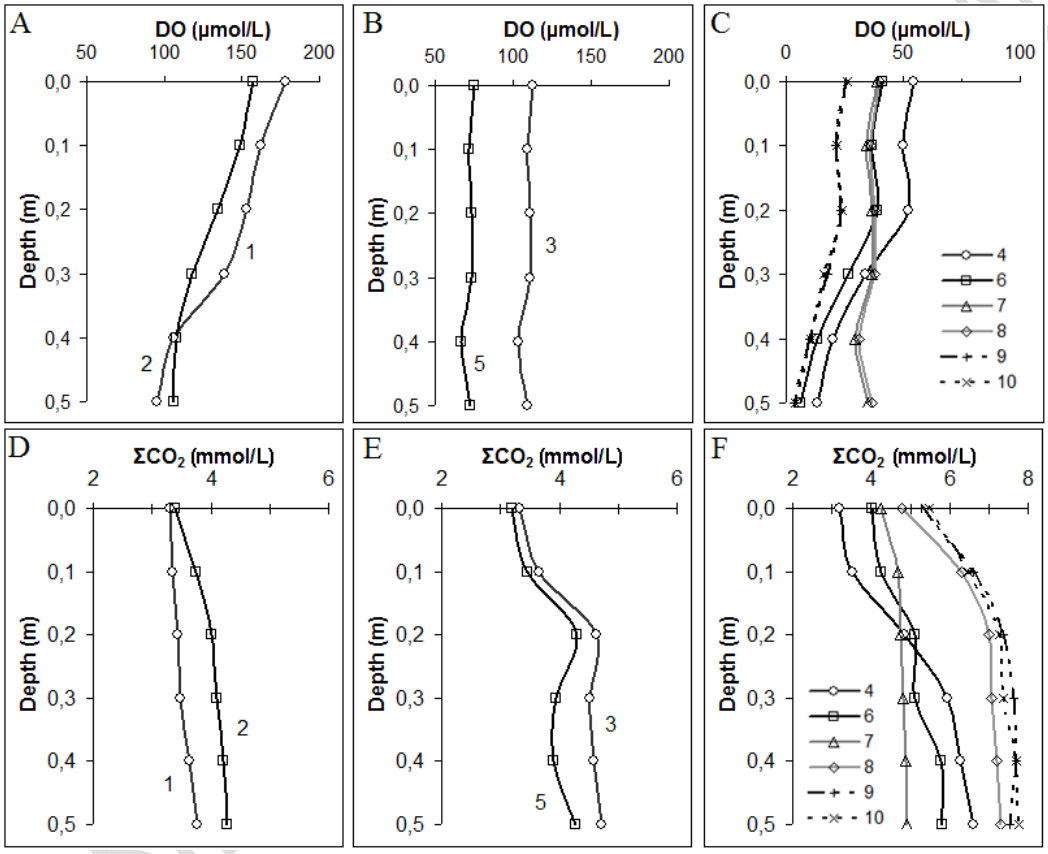

Fig. 4. Vertical profile of DO (µmol/L) and ΣCO_2 (mmol/L) according to the zoning process: A) and D) outer shelf; B) and E) inner shelf; C) and F) coastal zone.

4.4. Sedimentary incubation

Incubation tests can be classified into open and closed systems. In the open system the loss of CO_2 by diffusion is allowed, which does not return to the system. However, the closed system is often questioned by 'imprisoning' the gases, preventing the changes at the water-sediment interface. The fact is that both tests have positive and negative points, and it must be assumed that there is an imprecision in the results. The great trump of incubation tests,

however, is the ability to quantitatively estimate the processes involved. It is based on this perspective that a closed test was applied to estimate the net productivity and mineralization content of OM in the coastal zone and ACS.

The variation of the CO_{2T} and O_2 in the waters ($\Delta CO_{2T}(t)$ and $\Delta O_2(t)$), including the pore waters, is controlled not only by the biological processes but also by the diffusion rate of the gases in the interface zone ($\Delta(CO_{2T})_a$ and $\Delta(O_2)_a$), and the facilitation or not of the gas flow as a function of the degree of sedimentary porosity. Thus, the study of the diagenetic processes involving the production and mineralization from the CO_2 and O_2 variations in the water should be understood as an estimate, since there are several factors controlling the concentration and flow of these gases in the sediments, including hydrodynamics and seasonality. The closed incubation technique attempts to minimize the problem of gas exchange. Despite this, incubation reduces the flow of biogenic elements. The system's buffering capacity is of great relevance to the results, since any change in pH and alkalinity, especially alkalinity of carbonate (Alc_c), interferes with the concentrations of H_2CO_3, HCO_3^- and CO_3^{2-}, and consequently with CO_{2T} levels. It is tried to minimize this variation, considering that the chemical reactions and the diffusions present kinetics of the same order. Thus, when CO_2 adsorption occurs, a part of the CO_2 that enters the system is transformed into carbonates, and when the CO_2 desorption occurs, a fraction of carbonates from the system is converted into CO_2. Incubation tests confirmed that the range of 0.0 – 0.2 m is essentially the most active from the point of view of sediment reworking by the flow and inflow of the dissolved gases. As expected, CO_{2T} rates increased rapidly during the incubation period. Increasing the concentration of inorganic carbon forms may mean an increase in aerobic decomposition rates (complete decomposition), due to the increase in the supply of reactive organic compounds. Generally, the saturation of mineral carbonates and other forms of inorganic carbon are quite high in the sediments from ACS, as were observed by [2,12].

In the comparison of the results between the incubation of sediments from site 1, sandy and under strong influence by marine currents, to site 4, mud and located in protected area with marked sedimentation, the amplitude of variation for the incubation period ($t_0 \rightarrow t_{96}$) was much higher at site 4. The ΔCO_{2T} determined were respectively; site 1= 1.44 mmol/L and site 4= 4.94 mmol/L (Table 4), suggesting that the net mineralization exceeded the net production of organic matter to [$\Delta(CO_{2T})_b > 0$ for $\Delta(O_2)_b < 0$]. The coefficient of activity (I) also showed a greater amplitude of variation in site 4 (ΔI= 3.26 meq/L) compared to site 1 (ΔI= 1.81 meq/L). The activity coefficient is a function not only of the chemical species present, but also of the ionic interactions in pore water. In silica sediments, the ionic interactions are weak and easily disrupted by the current underflow, which eventually penetrates the sediments due to their high porosity. Already in silt-clayey and clay-silty sediments, the low porosity (<0.7 ml/cm^3) reduces the mobility of the mineral elements, accentuating the ionic interactions, which present strong connections, especially cationic, with the negative external surface of the particles of clay and organic matter. The ionic forces (F_i), determined as a function of their logarithms, followed the same trends, being greater in the mud sediments. These behaviors are confirmed in the CEC analysis. Another important aspect is the variation rate in the productivity of NH_4^+ ions (Table 4), which showed influx in sandy sediments (site 1 = -9 µmol/L), and high efflux for mud sediments (site 4 = 53 µmol/L).

Extrapolating the results of the incubation test to the study area, it is possible to establish some hypotheses: 1) the flow of marine currents at site 1 may be allowing the aerobic oxidation in these sedimentary layers, with the nitrification route more pronounced than the ammonification rote; 2) in the region of the coastal zone and inner shelf the routes of oxidation and reduction may be alternating according to the physical, physical-chemical and

seasonal factors; 3) in the coastal zone and inner shelf the net mineralization rate has exceeded the net production rate of organic matter, since the calculations show $\Delta(CO_{2T}) > 0$ for $\Delta(O_2) < 0$ (Table 4) for the vector from site 1 to site 4 (Figure 1). It should be considered, however, that the rate of sedimentation or continuous contribution of sediments from the Amazon River to the inner shelf is immense, as already discussed.

Daily fluctuations in the rate of NH_4^+ production at the same site, with changes in the axis of orientation of influx - efflux (nitrification/ammonification) are not uncommon, having been observed even in incubation tests [29,30]. In the specific case of the sediments located in the axis of orientation of the vector shown in figure 1, it is believed that the great difference in porosity and OM contents of the sediments, associated to the depth of the layer, were the predominant factors in the change of the orientation axis of inflow-efflux. This was confirmed by determination of iron fractions. Most of the time Fe^{2+}/Fe^{3+} ratio was <1.0 throughout the sedimentary profile (Figure 5), suggesting a mild to moderate oxidation pattern in the first 0.4 m, especially for outer shelf sites (sampling sites 1 and 2). A sensitive reduction in the degree of oxidation of the ferric ions was observed in sites 2 and 3 from 0.4 m. However, site 4 (Silt + Clay> 80%) presented higher iron ratio, with Fe^{2+}/Fe^{3+}> 1.0, indicating a predominance of the maintenance of the reduced form of iron (Fe^{2+}), which by electric affinity remains in the sedimentary layer adsorbed the particles of clay minerals and organic compounds not totally mineralized. Metal profiles sensitive to oxidation variation, such as Fe and Mn, may indicate redox potential changes within the sedimentary layers, being influenced by the concentration of DO in the pore water. The pore water column can define alternate zones of oxidation and reduction of chemical species as a function of depth, according to sedimentation rates, oxygen demand, nutrients and microbiological processes [34]. The processes of dissolution and precipitation of minerals can affect the nutrient concentration (C, N and P) and trace elements in the sediments [8], because these chemical species may be being adsorbed by the surface of minerals as iron oxides and hydroxides. The behavior of the trace elements in the bottom sediments is strongly associated with organic matter rates; pH (increase of the pH implies increase of the metallic adsorption); O_2 content; redox potential; seasonality (flow of alternating currents); and diagenetic processes, which occur in the fluvial-marine system. In this case, three routes of adsorption of trace elements to the iron in the sediments and pore water can be established, taking into account the depth and oxygen content: 1) adsorption in Fe^{3+} oxides and hydroxides, especially at the water-sediment interface and with increased metal mobility; 2) dissolution of Fe^{2+} oxides and hydroxides in the layers of less interference of O_2, in this case the trace elements may follow the oxidative route towards the interface, or to stay associated with reduced forms (S^{2-}) and follow the co-precipitation way; and 3) fixation on the mineral surface or precipitation in the autigenic mineral phase, in or near the anoxic environment (Figure 5). Reactive trace elements such as Cu, Ni and Zn may have their concentrations controlled by co-precipitation with Fe sulfides, which would result in the reduction of the metallic mobility of these elements. Comparing the trace element contents with the vertical distribution profile of the iron fractions, it was possible to evidence an increase in trace element concentrations in Fe reduction zones, indicating processes of desorption of iron oxides and hydroxides, and mineralization of organic matter.

Table 4. Estimates of net production and net mineralization of organic matter from the incubation test (t= 96h) for sites 1 (outer shelf) and 4 (coastal zone).

Site	Depth (m)	$[CO_{2T}]$ (mmol/L)		ΔCO_{2T} (mmol/L)	ΔI^* (meq/L)	F_i** (log)	ΔNH_4^+ (µmol/L)	Fe^{2+}/Fe^{3+}
		t_0	t_{96}					
1	0.0	3.30	4.10	1.44	1.81	-1.50	-9	0.35

1	0.5	3.50	4.80					0.54
4	0.0	3.60	6.60	4.94	3.26	-0.48	53	0.65
4	0.5	3.80	8.70					1.45

*Activity coefficient variation for t=96h
**Ionic force defined by [19]

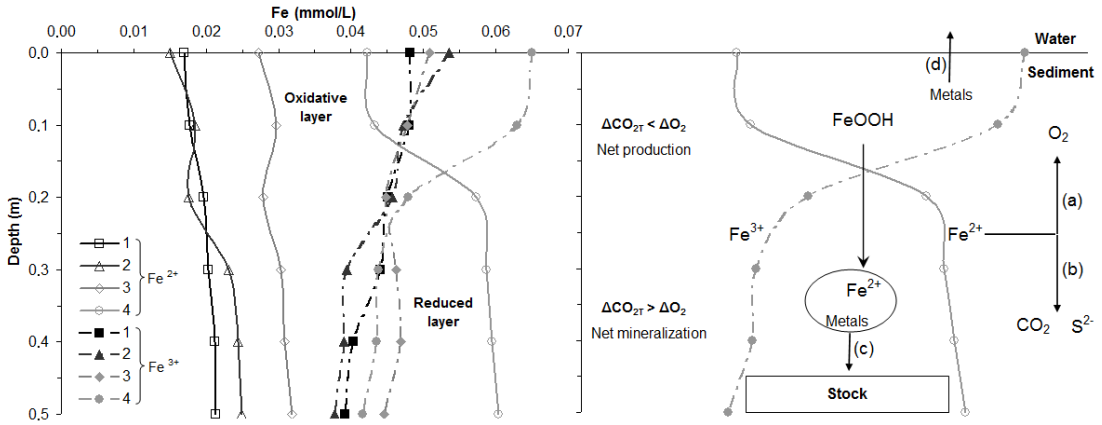

Fig. 5. Vertical profile of the Fe^{2+} and Fe^{3+} fractions in the pore water from sediments located in the vector 1 – 4 of the ACS, and indication of the possible transport routes of the associated trace elements. Legend: a) decomplexing; b) co-precipitation; c) fixation; d) mobilization.

5. CONCLUSION

Establishing that the study area is comprised between the coastal zone, which receives directly the sedimentary contribution from the discharges of the Amazonas and Pará rivers, and the outer shelf, which is under direct influence of the ocean currents (see Figure 1), was able to the following conclusions: 1) There is a strong zonation in the sedimentary transport and deposition processes, influenced by the granulometry and texture of the sediments, and the fluvial-marine currents, which alternate in direction seasonality. Thus, it was possible to identify that the sediments of the coastal zone and inner shelf are predominantly silt-clayey and clay-silty as opposed to sandy and sand-silt sediments of the outer shelf. 2) The trace elements presented a distribution and concentration pattern equivalent to that of the sedimentary distribution pattern, with higher metallic contents in the deposits of clay and organic matter of the coastal zone and inner shelf. 3) The determination of a weight factor (F_w) calculated to estimate the degree of importance of each physical and physical-chemical parameter in the distribution and mobility of trace elements showed that these elements were strongly related to the depth and location of sampling sites, sand, clay, OM and OC levels, and DO concentration, especially to Cr, Ni and Zn metals. 4) The vertical distribution of O_2 and CO_2 and the Fe^{2+}/Fe^{3+} ratio in the pore water suggest a predominance of organic matter oxidation in the sedimentary layer between 0.0 and 0.2 m, with partially anaerobic mineralization of the mud sediments below 0.4 m, especially in the coastal zone and inner shelf. However, the results indicate that there may be very significant differences between aerobic and anaerobic degradation of organic matter. 5) Increases in trace element concentrations were observed in Fe reduction zones, indicating processes of desorption of Fe oxides and hydroxides and net mineralization of OM. 6) The results of the incubation test indicated that $\Delta(CO_{2T}) > 0$ for $\Delta(O_2) < 0$, suggesting that especially for the coastal zone and

inner shelf the net mineralization rate has exceeded the net production rate of organic matter.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

AUTHORS' CONTRIBUTIONS

All authors participated of the samples collection, date and statistical analysis and wrote the first draft of the manuscript.

CONSENT

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ETHICAL APPROVAL

This section is not applicable in this manuscript.

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