Bol. Inst. Oceanogr. Venezuela, 53 (2): 79-93 (2014) 9 Figs.

GEOCHEMICAL CHARACTERISTICS OF SURFACE SEDIMENTS FROM THE MARINE-COASTAL REGION NORTH AND SOUTH OF THE PARIA PENINSULA, VENEZUELA

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ABSTRACT: Environmental characteristics of the Northern Platform of the Paria Peninsula (PP) and the Paria Gulf (GP) are caused by water flow and sediment of the Orinoco river, the ocean currents that move along the eastern coast of South America transporting a large quantity of sediment from the Amazon river, the tidal action, waves and the current regime of the continental shelf including coastal upwelling induced by trade winds. All these factors affect biogeochemical processes in sediments that have different sources and conditions of transport, sedimentation and preservation. Accordingly, it raises as fundamental objective of this paper to describe some environmental parameters of bottom water and some geochemical characteristics such as texture, mineralogy and organic carbon content (Corg), sulfur (S), total phosphorus (TP) and total nitrogen (TN) from surface sediments of the study region. The texture was performed according to the modified pipette method and mineralogy by X-ray diffraction. The Corg was determined by dry combustion technique after acid attack, S by EA-ICP, while the PT and NT by the method of Valderrama (1981). Iso-concentration maps for the distribution of these parameters on the continental shelf north of the Peninsula (PP) and Gulf of Paria (GP) were prepared. In general, the sediment has a texture or grain size of sandy-loam and sandy-silty type, mineralogical composition consists of quartz, muscovite, kaolinite, calcite for some PP stations and zircon for GP, making mineral distinctive environments sedimentation and sediment source. The average concentrations were Corg 1.53%, S 0.23%, PT 0.04% and NT 0.03%. Ocean currents and coastal upwelling patterns may influence the spatial distribution of these variables. There is an effect on the production, distribution and sedimentation of OM in the study area, caused by the discharge of the Orinoco and Amazon River through the flow of Guyana, which directly impacts surface waters and sediments of the Paria Gulf. These results allow distinguishing two environments of sedimentation with suspended matter inputs from different sources. The PP surface sediments with typical characteristics of coastal marine sediment with input from autochthonous organic matter, resulting from primary productivity that are influenced by the phenomenon of coastal upwelling. There is greater variability in the GP, indicating different sources of sediment that result in a mixture, confirming the contributions of the Orinoco and Amazon River. The GP provides marine environments, transitional and continental. In the other hand, the PP only provides marine environments that lead to differentiation in composition, texture, mineralogy and distribution between the two regions. Sea currents and the source of the sediment may be the most important factors controlling the spatial distribution of sediments and the elements considered in the region.

Keywords: Marine Surface Sediments, Organic Carbon, Nitrogen, Phosphorus, Sulphur.

RESUMEN: Las características ambientales de la Plataforma Norte de la Península de Paria (PP) y el Golfo de Paria (GP) son causadas por el flujo de agua y los sedimentos de los ríos Orinoco, las corrientes oceánicas que se mueven a lo largo de la costa oriental de América del Sur transportar una gran cantidad de sedimentos de la Amazonía, la acción de las mareas, las olas y el actual régimen de la plataforma continental y la surgencia costera inducida por los vientos alisios. Todos estos factores afectan a los procesos biogeoquímicos en sedimentos que tienen fuentes diferentes y las condiciones de transporte, sedimentación y preservación. En consecuencia, se plantea como objetivo fundamental de este trabajo se describen algunos parámetros ambientales del agua de fondo y algunas características geoquímicas como la textura, mineralogía y el contenido de carbono orgánico (Corg), azufre (S), fósforo total (PT) y el nitrógeno total (NT) de sedimentos superficiales de la región de estudio. La textura se realizó de acuerdo con el método de la pipeta modificado, la mineralogía por difracción de rayos X, Corg se determinó por la técnica de combustión seca (previo ataque ácido para eliminar carbonatos), Azufre (S) por EA-ICP, mientras que el PT y NT mediante el método de Valderrama (1981). Se prepararon mapas de iso-concentración de la distribución de estos parámetros en la plataforma continental del norte de la Península (PP) y el Golfo de Paria (GP). En general, el sedimento tiene un tamaño de grano o textura de tipo arenoso y areno-limosa, la composición mineralógica consiste en cuarzo, moscovita, caolinita, calcita para algunas estaciones de la PP y circón para el GP, marcando entornos distintos de sedimentación mineral y diferentes fuentes de sedimentos. Las concentraciones medias fueron Corg 1,53%, 0,23% S,% PT NT 0,04 y 0,03%. Las corrientes oceánicas y costeras y los patrones de afloramiento pueden influir en la distribución espacial de estas variables. Hay un efecto sobre la producción, la distribución y la sedimentación de la materia orgánica en el área de estudio, causada por la descarga del río Orinoco y el Amazonas a través del flujo de Guyana, que afecta directamente a las aguas superficiales y sedimentos del Golfo de Paria. Estos resultados permiten distinguir dos ambientes de sedimentación con aportes de materia a partir de diferentes fuentes. Los sedimentos superficiales PP con características típicas de los sedimentos marinos costeros con el aporte de materia orgánica autóctona, como resultado de la productividad primaria que influenciado por el fenómeno de surgencia costera. En la PP hay una mayor variabilidad, indicando las diferentes fuentes de sedimentos que dan lugar a una mezcla, lo que confirma la contribución del Orinoco y el río Amazonas. El GP tiene la influencia de tres ambientes diferentes: marino, de transición y continentales. Mientras que, el PP sólo tiene la influencia del ambiente marino. Esto da lugar a diferencias entre la composición química, textura, mineralogía y sus distribuciones dentro de las dos regiones. Las corrientes marinas y la fuente de los sedimentos pueden ser los factores más importantes que controlan la distribución espacial de los sedimentos y los elementos considerados en la región.

Palabras clave: sedimentos marinos superficiales, carbono orgánico, nitrógeno, fósforo, azufre.

INTRODUCTION

Several investigations of coastal sediments have shown that these ecosystems are extremely fertile with high organic productivity, product of coastal dynamics such as upwelling and continental inputs from rivers, which can provide a large supply of nutrients (GOMEZ 1996; ODRIOZOLA 2004; BENITEZ & OKUDA 1976; MOIGIS & BONILLA 1988; MONENTE 1989, 1990,1997). On the northeastern coast of Venezuela, upwelling phenomena occur due to the action of trade winds during the first months of the year. This affects the hydrodynamics of the entire area and contributes to fertility as a result of increased concentrations of nutrients in the surface layer, resulting in a *short time-lag* to *phytoplankton* growth. During the rainy season, nutrient inputs from the Orinoco and Amazon rivers that reach this region due to sea water circulation, promote high organic productivity (GOMEZ 1996; ODRIOZOLA 2004; BENITEZ & OKUDA 1976; MOIGIS & BONILLA 1988; MONENTE 1989, 1990,1997).

The marine sediment is defined as an aggregate of untold numbers of insoluble particles of unconsolidated material, which have been transported to the bottom of the oceans and seas by various transport agents. These sediments are the ultimate repository of most of the waste generated by man, and can thus be used as sensitive indicators for monitoring the spatial and temporal distribution of pollutants (BALLS *et al.*1997; KISH & MACHIWA 2003). They also provide information on the geochemical changes that occur over time in these environments and can be used to establish baseline levels in a particular area (DASSENAKIS *ET AL*.1997; RUBIO *et al.*2000; TUNCER *et al.* 2001).

Thus, the characterization of sediments is of some importance in oceanography and geochemistry and may help us to understand certain phenomena such as the distribution of contaminants and their relationship to the geochemical and hydrodynamic characteristics of each marine region (HELING *et al.*1990). The nature, size distribution and some physicochemical characteristics of marine sediments may help understand the current system, the baseline redox condition, the activity of microorganisms and the nature of the sedimentary deposits (BONILLA *et al.*2003)

According to GOMEZ (1996), the waters of the Caribbean are generally poor with a few moderately fertile areas, such as those close to northeastern Venezuela. Regional enrichment is commonly associated with the upwelling of subsurface waters, an annual hydrographic phenomenon that occurs during the first few months of the year. However, the possibility of the existence of factors that promote water fertility throughout the year has been raised. The great South American rivers (Orinoco and Amazon) and internal waves bring nutrients, thus producing eutrophication of the waters of coastal lagoons such as La Restinga (Margarita Island) from May to November, when upwelling becomes less intense or ceases altogether. MONENTE (1997) attributes changes in the composition of the surface waters of the Caribbean to variations in the flow of the Orinoco and Amazon rivers throughout the year, as well as efficient geochemical processes that operate between the mouths of these rivers and the Caribbean Sea. Other processes that occur in upwelling zones near the coast of Venezuela have already been mentioned. Regardless of the importance or likely importance of the above mentioned phenomena, there are others that also contribute significantly to the enrichment of these waters. East of 63 º west longitude there is an important upwelling zone close to the coast as well as downwelling, causing rearrangement of the surface layers in the first 100 meters. This process is not continuous and is interspersed with waters of continental origin. These two phenomena together contribute significantly to the enrichment of surface water bodies. They are not continuous, however, but rather occurr intermittently throughout the year in a pulse-like fashion.

The marine area on the Northern Peninsula of Paria Platform (PP) is a small portion of the southeastern Caribbean Sea, lies entirely within the continental shelf, so to find relatively shallow depths across the study area. This presents a depths ranging from 37 m near Margarita to 110 m near Trinidad and has a length of 100 km and a width of 35 Km. Geomorphologically, the Gulf of Paria (GP) is a shallow inland sea between the east coast of Venezuela and the island of Trinidad and is made up of different regions formed by estuaries, deltas and platforms, which are important in the sedimentation of the Gulf. (Okuda *et al.* 1974)

The environmental characteristics of Paria Peninsula (PP) and GP are the result of the flow of water and sediments of the Orinoco River, the ocean currents that move along the east coast of South America and carry a significant amount of sediment from the Amazon River, the action of tides, waves and currents regime of the continental shelf and coastal upwelling regime determined by the action of the trade winds. All these factors affect the physical and chemical processes in the sediments. Therefore, the organic matter present in this medium has different sources and transport conditions, sedimentation and preservation are different. There is a wide range of interests so studying the marine sediment, so that the main objective of this paper is to evaluate some variables geochemical of surface sediments from the marine coastal area north and south of the Paria peninsula.

MATERIALS AND METHODS

Sampling

Sediment samples were collected at 44 stations established throughout the study area, 24 in the PP and 20 in the GP (Figure 1), during an oceanographic survey

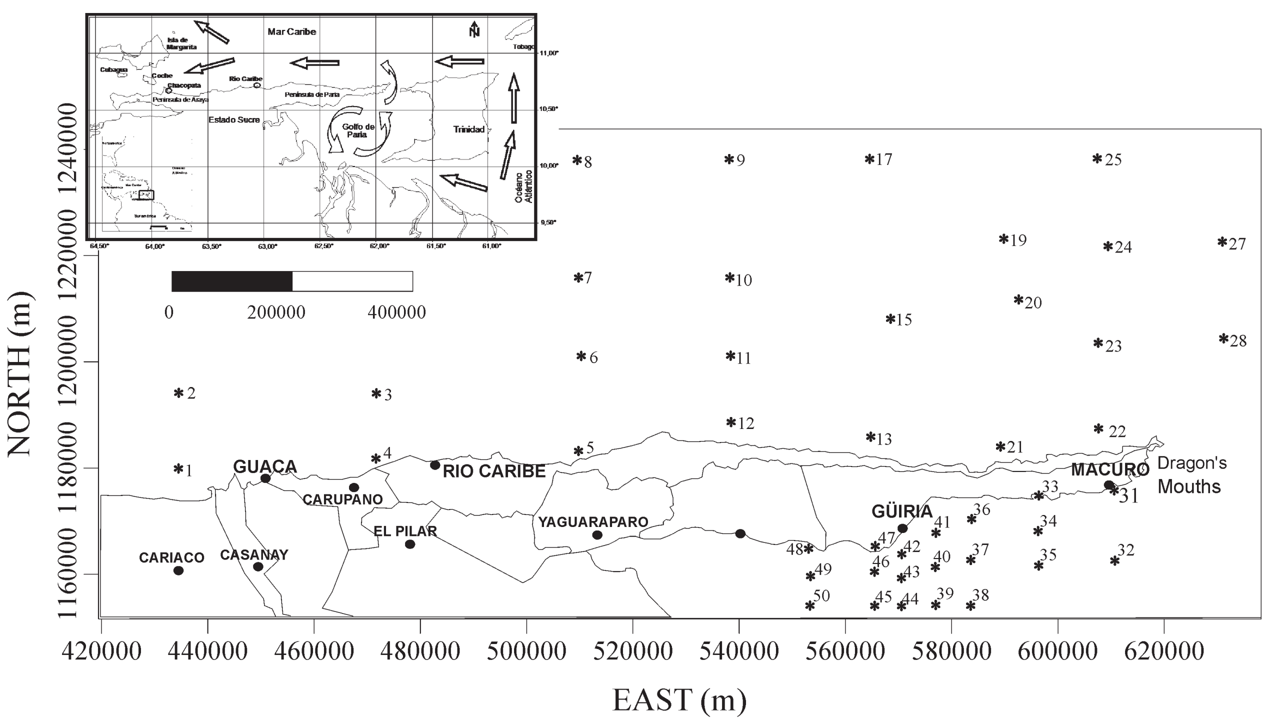

Fig. 1.- Study area in the coastal marine region north and south of the Paria Peninsula, Venezuela.

was conducted aboard the research vessel "Guaiqueri II" in October 2005. The positioning of the vessel was performed at each station using GPS differential corrections transmitted by satellite, ensuring accuracy in the position less than a meter. For this sampling rate is used a dredger Pettersen subsamples were processed and stored in function of the different analysis to be performed.

Sediment Texture

The separation of size fractions of sediments was carried out in two stages: firstly the gravel and sand fractions were separated from the mud fraction (silt and clay) by wet sieving after drying and weighing the samples, and secondly, the silts were separated from the clays using a modification of the pipette method. This procedure is based on the rate of sedimentation of grains over different time intervals, according to Stokes' Law Roa & Berthois (1975). Once separated, the two fractions were subjected to mild heating to evaporate most of the water and then left at ambient temperature. The fractions were then quantified by weighing.

Mineral composition

To determine the mineral composition of the sediments was used the technique of X-ray Diffraction, using a Powder Diffractometer (D8I) Bruker brand, model D8 advance with anticathode Cu, voltage 35 kV, current 25 mA, 2è angle from 2 to 88, normal window, a goniometer 0.1 rate of 3 deg / sec. It took approximately 1 g of dry sediment, previously pulverized in agate mortar and mounted, as homogeneous as possible, in the sample holder of the team, then underwent XR incidence of approximately 26 minutes and the diffractograms were obtained, which were then interpreted with the computer program EVA and cards for each mineral.

Organic carbon

Corg was determined by first applying an acid attack to the samples in order to eliminate carbonates. The samples were then dry-combusted with a LECO C-144 analyzer. We assumed that the carbon measured was associated solely with the organic matter in the sediment, the fraction that had not reacted with the acid.

Total sulfur

The determination of S was carried out with a modification of the methodologies presented by Tessier *et al*. (1979), described in Roux *et al.* (1998) and Izquierdo *et al*. (1997) for the fraction 4, with the atomic emission technique inductively coupled plasma (ICP-OE).

Phosphorus and total nitrogen

Total P and N were determined using the method described by Valderrama (1981), based on the simultaneous oxidation of nitrogen and phosphorus compounds in the samples and the resulting solution used for both analyses. The phosphorus content was determined following the method of Murphy & Riley (1962). Nitrogen content was ascertained by passing a 4ml aliquot through a Technicon autoanalyzer II, with a Scientific Instruments detector AC-100, which reduced NO_3 to NO_2, and recording the resulting concentrations. Total N content was calculated stoichiometrically from the nitrite concentration recorded.

RESULTS AND DISCUSSION

Bathymetry, temperature, dissolved oxygen and fluorescence index in bottom waters

These parameters were taken from the Environmental Baseline Mariscal Sucre Project: Abiotic Components. Final Report, Volume II, which provides data from an integrated study of the environmental characteristics of the coastal marine environment in the northern of the Paria Peninsula continental shelf and the northwest sector of the Gulf of Paria.

The seafloor morphology commonly controls the textural distribution of sediments and the geochemistry of benthic micro and macronutrients in coastal and oceanic environments (Burone *et al.* 2003; Escobar-Briones & Garcia-Villalobos 2009; Silva & Astorga 2010). Figure 2A shows the bathymetric distribution of the region. Within the study area, the shallowest sediments were in the GP, specifically in the coastal zone where they were only to 4.1 m deep, while maximum sediment depths were recorded for the PP, northeast of the coast, where they reached 144.4 m deep opposite Dragon's Mouths.

In the study are the bottom water temperatures (Figure 2B) are influenced by Atlantic waters flowing through the passage between Trinidad and Tobago and those coming from inner the GP. These waters show a temperature range between 21.38 °C and 30.94 °C with colder water entering from the northeast to the PP and warmer waters located in the GP, due to its lower depth and inputs from the Orinoco River.

Dissolved oxygen in water comes from many sources, the main one being oxygen absorbed from the atmosphere.

The surf allows water to absorb more oxygen. Physical, chemical and biological processes induce the exchange of oxygen across the air-ocean interface (Redfield 1942). Figure 3A shows the distribution of dissolved oxygen in the bottom waters from study area. Oxygen concentrations lower than 2.75 ml l^{-1} were found in the waters towards the central sector of PP area, which then increase to a peak of above 3.25 ml l^{-1} in the northeastern sector. In the GP, oxygen concentrations were below 2 ml l^{-1} in areas furthest from the shore. These low values are due to processes such as heterotrophic respiration and the bacterial oxidation of organic matter (OM).

The fluorescence is attributed to the emission of the energy absorbed by the chlorophyll of photosynthetic pigments (Ostrowska *et al.* 2000). The fluorescence index (FI) is used as an indicator of phytoplankton biomass. Many authors have shown that the FI is well correlated

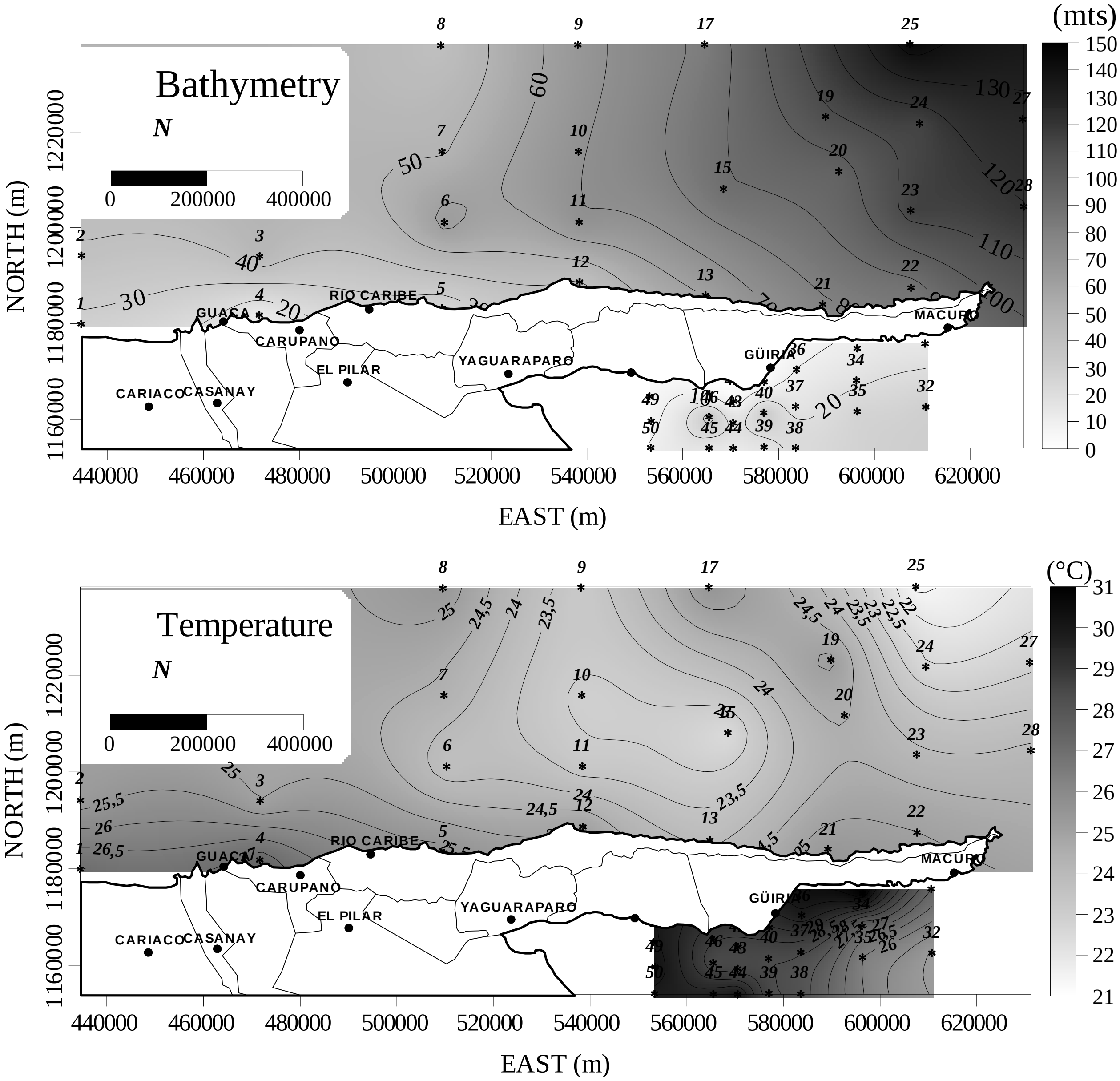

Fig. 2.- a) Bathymetry of the study area; b) bottom water temperature in the study area.

with chlorophyll concentration in water bodies. The bottom waters of the northern PP continental shelf had higher FI values towards the west (Figure 3B) and were higher than 1.5 units between the towns of Carúpano and Morro de Puerto Santo, suggesting that there was considerable biological activity in the waters of this region at the time of sampling. To the east, the bottom waters showed low phytoplankton activity, possibly because of a higher proportion of suspended matter due to tidal influences at Dragon's Mouths. The waters of the Gulf of Paria are considered to be some of the least productive along the northeastern Venezuelan coast BENITEZ & OKUDA (1976). The differences between values reported at different times of the year may be attributed to seasonal variations in nutrient levels and the turbidity of the water MOIGIS & BONILLA (1988). In the Gulf of Paria, the highest values (higher than 1.5 units) were recorded towards the west of the study area (Figure 2D), suggesting significant

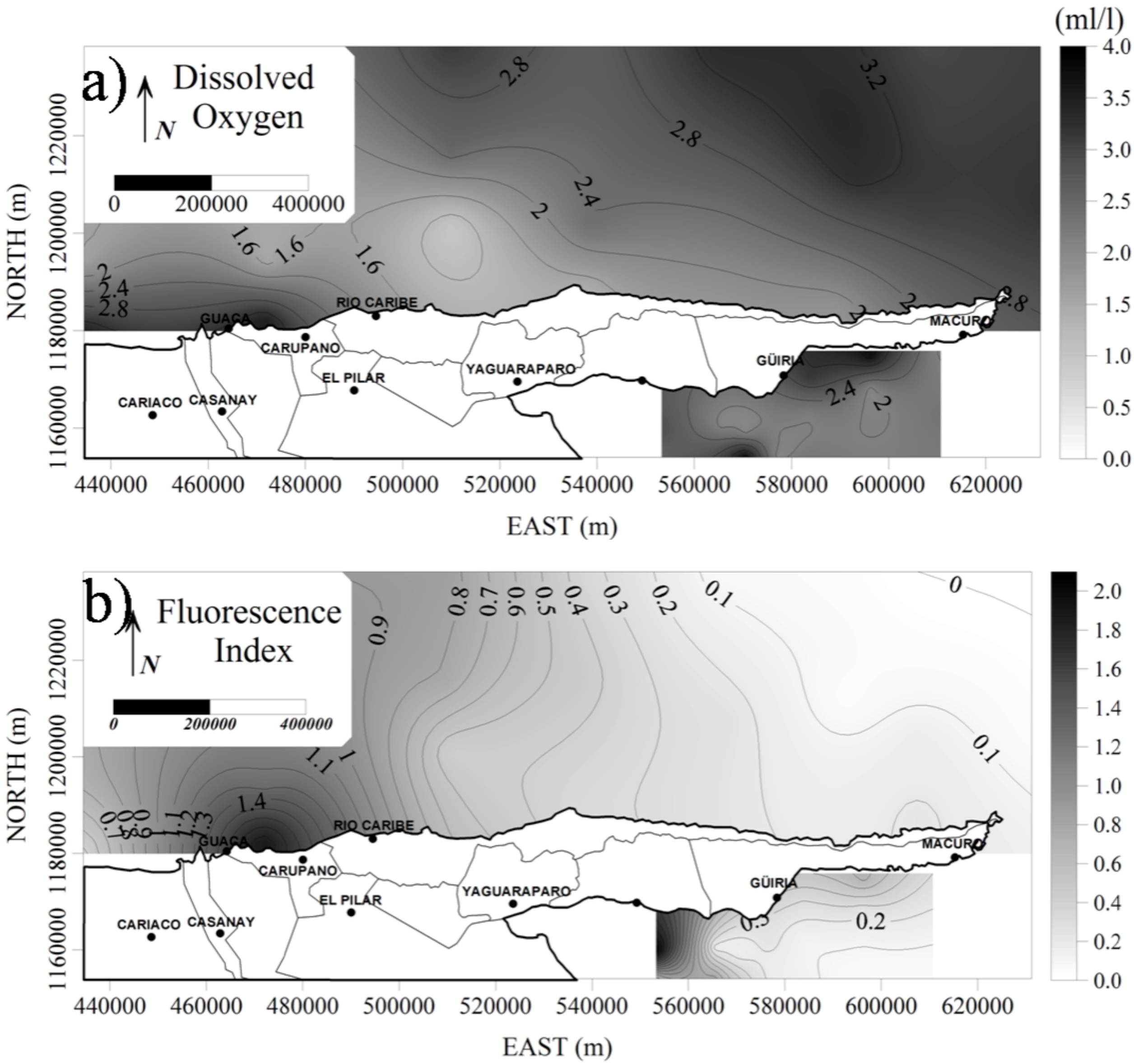

Fig. 3.- a) Dissolved oxygen of bottom waters in the study area; b) Fluorescence index of bottom waters of the study area.

phytoplankton activity compared with the other sampling sites. The rest of the Gulf showed low biological activity, with rates below 0.5 units although there was a slight increase in the area of Puerto de Hierro, west of Macuro, where values were slightly above 0.5 units.

Sediment texture

In order to evaluate the textural composition of the sediments of the study area was made a map of the spatial distribution of the different classifications of sediment in the study area (Figure 4). According to the results, the surface sediments of the PP and the GP have a mainly sandy loam texture. However, in the central area of the PP and the central-coastal area of the GP, the sediments have a sandy-silt texture, with the GP sediments having a higher proportion of fine grains (silt and clay). This texture is in concomitance with the suggested by Silva & Astorga (2010) for surface marine sediments of similar environments. This reflects the sediment dynamics prevalent in this coastal marine region, which promote the deposition of predominantly fine grained sediments, due to the geomorphology of the area and the flocculation of clays that occurs when seawater is mixed with fresh water from the Orinoco River.

The distribution of the different textural fractions in these regions is influenced by factors such as topography, speed and direction of winds and the various currents. In the PP contributions came from various sources: biogenic and terrigenous domestic effluents and rocky cliffs erosion of coastal margin, transported by continental runoff, also from the Amazon and Orinoco, the Guiana Current through the passage between Trinidad and Tobago and Snap dragon, the influence of the currents in the Caribbean that distribute these sediments, as well as those formed in situ along the shelf, wide estuaries and deltas that are part of a platform, has to contain sediments from the Orinoco Delta which are transported by the Caño Mánamo download and advection by waves and longshore currents via "Boca de Serpiente" (Warne *et al*. 2002). Of the total sediment entering the Gulf, a portion is transported to the southern Caribbean Sea, through of "Boca de Dragón" (Monente 1989, 1990). Milliman *et al*. (1982) estimated that approximately 2% of the sediments of the Orinoco and Amazon rivers, pass through Boca Dragon and are deposited on the continental shelf and the PP.

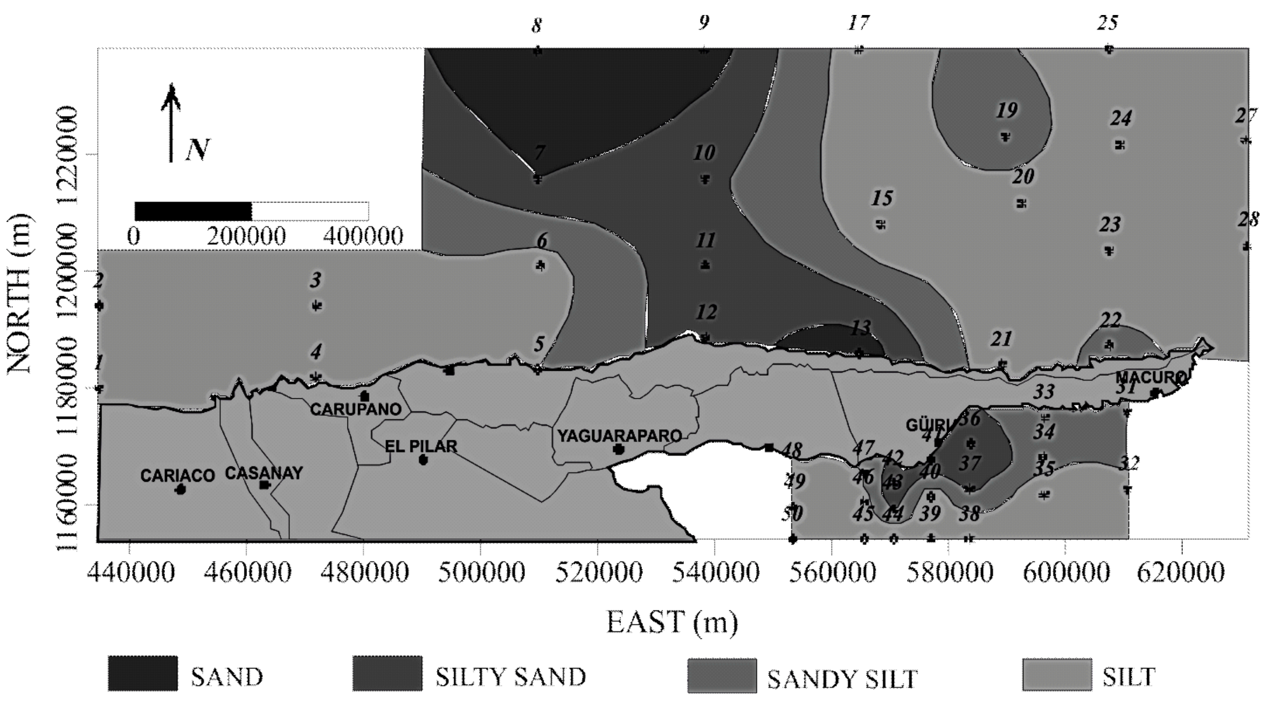

Fig. 4 .- Spatial distribution of the texture of the surface sediments of the study area.

Mineral composition

Sediment can be of organic origin and correspond to the remains of living organisms relatively abundant in this region or terrigenous continental origin, which are transported in suspension, by size or by river or coastal currents. Overall, the nature of these materials is highly variable because of the diversity and dynamic of transport agents: ocean currents, tidal currents, river runoff and wind. All this results in a great variety in the mineral composition of the sediment, which can be specified for each zone. To qualitatively assess the mineralogical composition of the sediments of the study area, we applied the technique of X-ray diffraction to silty fraction, obtaining diffractograms which show the presence of various minerals such as quartz, calcite, muscovite mica, clay minerals, among others. By getting the diffractograms of selected samples, it was observed that some follow similar diffraction patterns, which enabled researchers to facilitate the description of these sediments.

First have a group that describes the composition of the PP coastal sediment, as seen in Figure 5A, which presents the diffractograms for samples PMS (2) 1, 3, 4 and 22. In this group the composition is mainly dominated by quartz (SiO_2), kaolinite, feldspar and muscovite. It can be deduced that the sediment in the coastal area is predominantly terrigenous siliciclastic dragged by continental runoff, which form during the rainy season. Moreover, can not be excluded that the quartz from the PP can be microcrystalline biogenic, produced by phytoplankton and zooplankton organisms using it to their skeletons, and to die they sink into the seabed. Figure 5B shows the XRD patterns for the group of samples representing the north central region of the PP. In the same it can be observed that the mineral quartz remains the predominant fraction of excellence in this sediment. However, the mineral calcite appears representing marine influence in the composition of the sediments. Also are present kaolinite and muscovite. Microorganisms such as phytoplankton and zooplankton produce calcite from biogenic origin for their skeletons construction, so the calcite present in sediments may be due to a contribution of planktonic foraminifera native and / or calcareous remains of a coral formation near the area.

Finally, GP it was noted that all samples have the same mineral composition, only small variations in the proportion of representative minerals. Figure 5C shows the XRD patterns for some samples selected from the GP. This group shows that quartz is still the predominant mineral also appear kaolinite and muscovite. However, the GP XRD samples register the presence of zircon, the oldest known mineral on earth and one of the most abundant in the earth's crust (Wedepohl 1995). This mineral is the first product of crystallization of the igneous rock like granite or alkaline rocks and pegmatites. In sediments and altered grains are transported by erosion. It is considered a heavy mineral resistate and evidence in this case, the direct influence of continental contribution from the Orinoco River.

Organic carbon

The amount of Corg in marine sediment varies from < 0.1 % to > 30% and is often used as an indicator of the amount and type of organic matter that is deposited in the sediments from the water column. This Corg may have different sources of origin, so that in this study considered important to assess the Corg amount and distribution in sediments. The concentrations ranged from 1.29% to 10.06% with an average of 3.12%. It was observed that the highest values were located in the westernmost part of the PP (Figure 6), this can be the product of input of OM from continental (Demaison & Moore 1980; Tissot & Welte 1984; Silva & Astorga 2010). Marine OM inputs generated *in situ* due to higher organic productivity also contribute to the increase of OM in sediments. Moreover, low oxygenation conditions must exist, to preserve this material in the sediment. High values of Corg in the PP were found in shallower areas with high dissolved oxygen and FI values and coincide with an upwelling area, implying high primary productivity. This allows us to infer the conditions necessary for the production and accumulation of OM. In contrast, the central and easternmost of the PP shown low values, probably due to the transport and remineralization of the OM in the water column, that can produce carbon associated with slightly larger particle sizes, or particles that are not deposited in the sediment.

Meanwhile, despite the contribution of terrestrial OM from the Orinoco Delta and that brought by the Guyana Current from the Amazon, Corg values were low in the GP. According to Benitez & Okuda (1976), the waters of the GP should be considered some of the least productive along the northeastern coast of Venezuela. This is because this region is very shallow and influenced by different currents and water masses, which tend to cause mixing conditions and therefore oxidizing conditions unfavorable for the preservation of OM in the sediments. The high

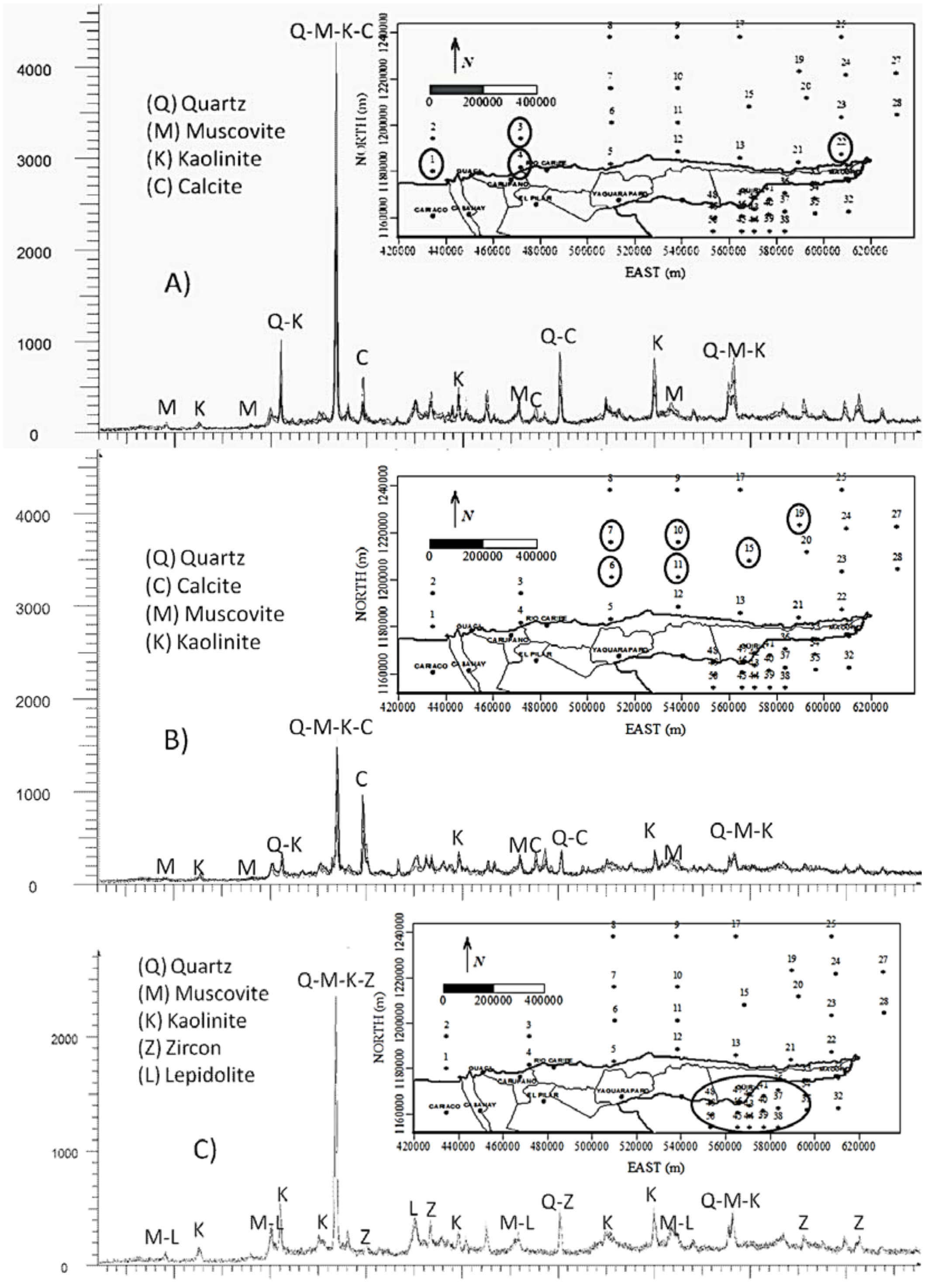

Fig. 5.- X-ray difractograms of mineral composition of sediments from the study area.

dissolved oxygen values found in the GP, and turbidity due to the suspension of fine material in the water column prevents the passage of sunlight, thus limiting photosynthetic processes and consequently the production of OM. The oscillation of the tides in the GP holds the fine material in suspension, which is then exported out to sea.

Total sulphur

Sulphur occurs in marine sediments chiefly as pyrite, which can form both directly or diagenetically with decomposition of organic matter in the sediment, or directly at the surface of the sediment when reducing and oxidizing conditions co-exist. Sulfur with Corg and other variables, can be an indicator of environmental conditions of sedimentation. For this and other reasons it is important to study sulphur in the marine environment, so then their concentrations and spatial distribution in the study area are discussed. Sulphur concentrations varied between 0.08 and 0.69% with an average of 0.23%. The spatial distribution observed for sulphur (Figure 7) was very similar to that of Corg and may reflect a relationship between them, with the highest values located at the westernmost north platform, that has been described so far as the most productive. In the GP the values found are lower than the PP, but are higher than those obtained in active sediments of some channels Orinoco River Delta, where the maximum values reported were of 3.20 ppm (YANES 1999).

High concentrations obtained may indicate deposition conditions slightly reducing the water-sediment interface, which favour the presence of microenvironments suitable for the formation and preservation of sulfur compounds. The highest values of sulphur, also associated with higher levels of Corg, confirm the high primary productivity of this area,. Also, take into account the influence of the Guyana current that transports terrestrial organic matter from the Amazon and Orinoco River and converge with the Equatorial current, creating conditions that favour an anoxic depositional environment, which allows the formation and preservation of compounds containing sulphur. Similar values were found in surface sediments of the Black Sea, which correspond to a typical anoxic (DIDYCK 1978). In the Black sea it is also observed reduction in the sulphur content to the deepest part of the platform, as seen in the GP, which indicate the changes in the environment of sedimentation, probably due to the circulation of different water mass. Other factors such as sedimentation rate, availability of sulfate and nature and amount of sedimentary OM have been found to be relevant for controlling the sulûdization and pyritization processes in these surface sediments (BILLON ET AL. 2001).

Phosphorus and total nitrogen

Phosphorus and nitrogen are important constituents of the marine environment. Their quantities can be limiting and influence the production or organic matter,

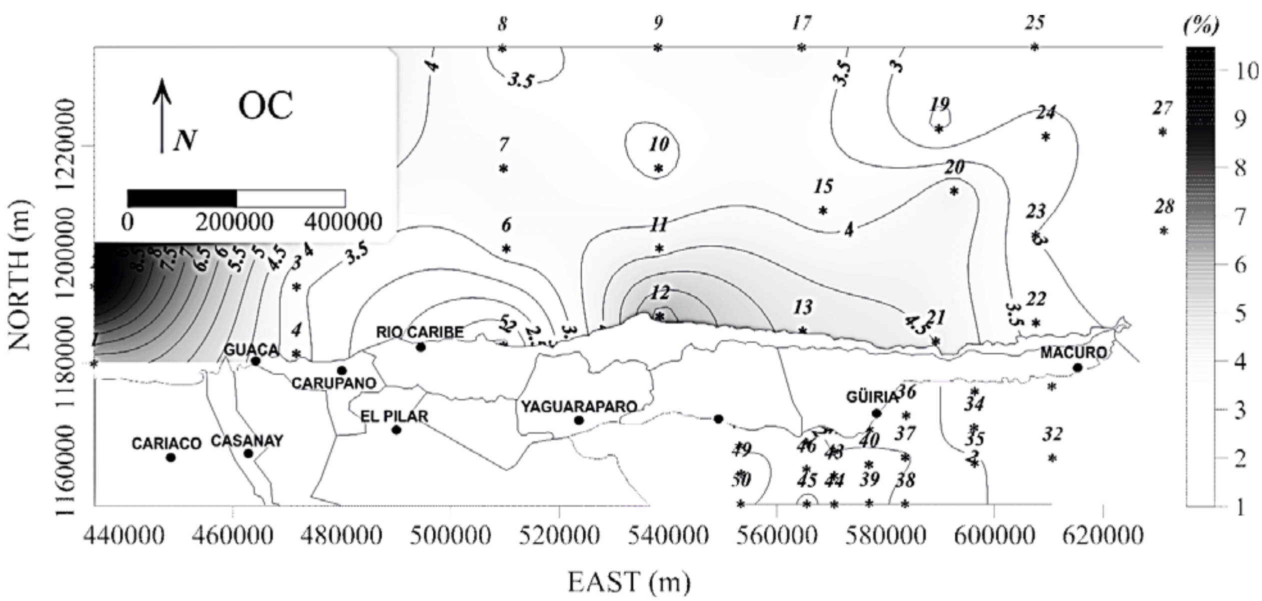

Fig. 6 .- Spatial distribution of Corg in the surface sediments from the study area

and their ratios can help determine the origin of the same. For this is important to assess phosphorus and nitrogen concentrations and spatial distribution in marine sediment from study area of this work. PT concentrations are between 0.02% and 0.44%, with an average of 0.08% and from 0.01% NT 0.70% with an average value of 0.16%. The Figures 8 and 9 shows the spatial distribution for TP and TN concentrations. Can observe that the GP and the central and easternmost of the PP have the lowest concentrations of TP, but increase gradually towards the westernmost of the PP where shown the highest values, thus coinciding with the Corg distribution.

The upwelling process and riverine inputs are considered a important source of TP to the marine coastal environments (Monbet *et al.* 2007). All the TP that is uptake for the phytoplankton and subsequent incorporated into organic matter aggregates and larger particles and then settle in benthic sediments.. In general, this particulate matter is remineralized at depth. In addition, zooplankton produce particles during feeding and excretion that settles to the deeper layers of the ocean leading to greater proportions of TP in the finer fractions of sediments. De La Lanza & Cáceres (1994) indicated that up to 60% of orthophosphates can be removed from the water by their adsorption in sediments, which could explain their high concentrations in coastal areas. The high concentrations of TP present in sediments reflect the ability or particular characteristics of the sediments to retain phosphorus, making it a significant internal source of P for coastal ecosystem that may play a critical role in buffering some chemical and ecological changes, which in turn promotes biotic and abiotic processes (Hou *et al* 2009; Wang & li 2010). Ponce *et al*. 2010 suggest that, benthic fluxes of phosphate are higher than diffusive fluxes, showing the importance of bioturbation processes on phosphate mobility at the sediment-water interface, as well as the importance of working with a high spatial resolution.

The main source of nitrogen in marine sediments is known to be organic matter released by the action of decomposing microorganisms. The microbial flora with the liberation of ammonia mineralizes the organic matter that accumulates in the form of particles. The clays present in the sediment can retain nitrogen due to cation exchange. Thus, the nitrogen affinity for the fine-grained fraction is due to the proportion of clay minerals present. However, the nitrogen quantity in sediments also is dependent on the amount of this ion in solution, the type of clay present and the presence of other ions in the pores of the sediment (Pellerin *et al.* 2004). In sediments, the processes of N fixation and P availability are influenced by a variety of environmental factors including water depth, the redox state of sediments, benthic primary production, pH and temperature (Joye

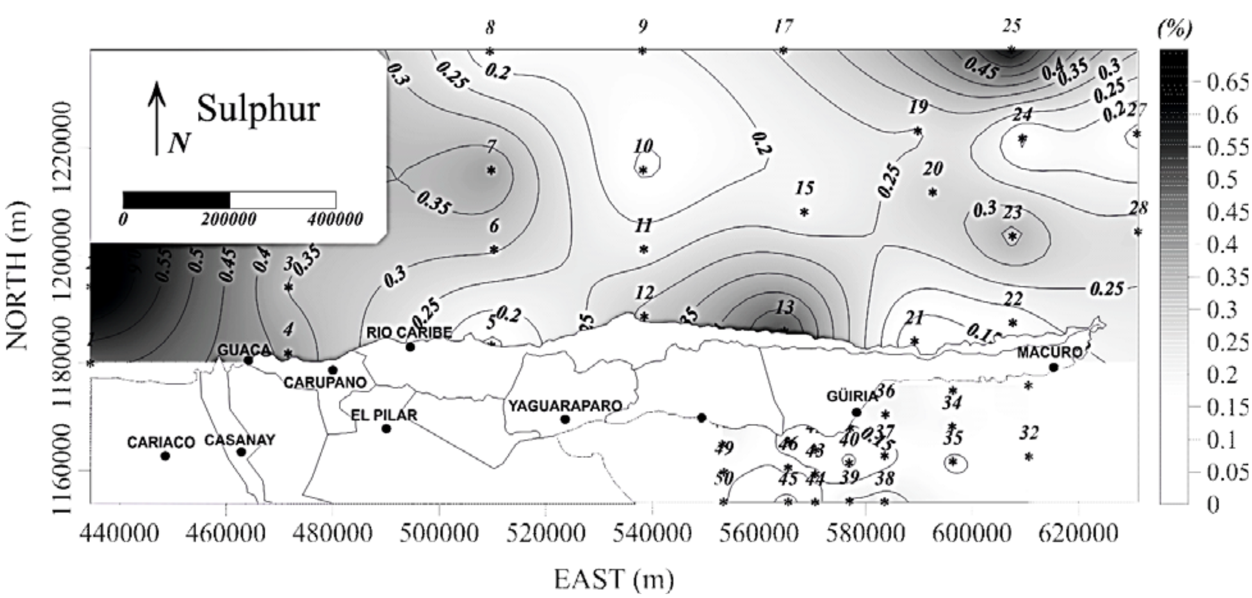

Fig. 7.- Spatial distribution of Sulphur in the surface sediments from the study area

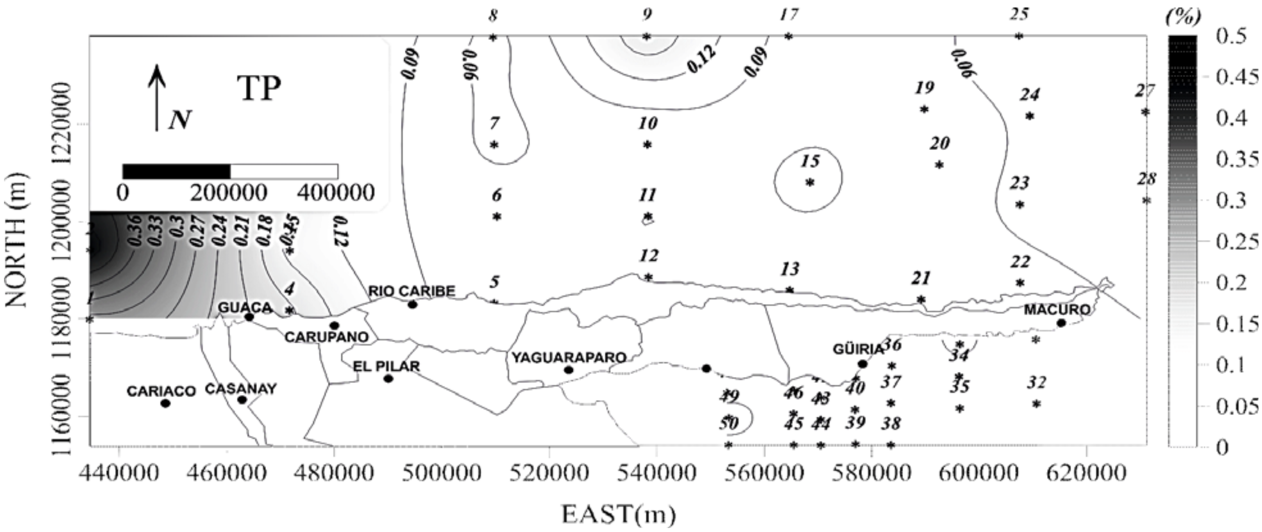

Fig. 8 .- Spatial distribution of TP in the surface sediments from the study area

& HOLLIBAUGH 1995; AN & JOYE 2001; GARDNER & MCCARTHY 2009).

The spatial distribution of these variables appears to be influenced by ocean currents and coastal upwelling patterns. The production, distribution and sedimentation of OM in the study area is affected by the discharge of the Orinoco River that impacts directly to the GP through numerous rivers and creeks, and the contributions of the Amazon River brought by the Guyana Current. Can note that there is a relationship between the content of Corg, P and N in the surface sediments to the study region. According to this arrangement, the greater the Corg content in the

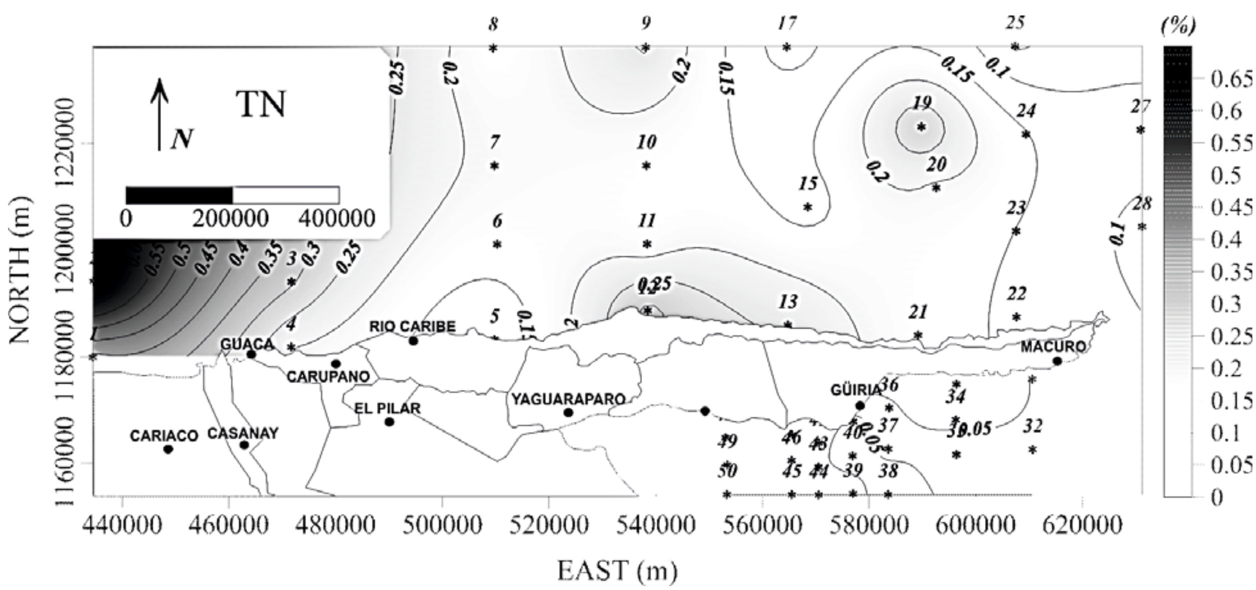

Fig. 9 .- Spatial distribution of TN in the surface sediments from the study area.

sediment, the higher the content of N and P total. According to this, the greater the Corg content in the sediment, is also high content of S, N and P total. According to these results, depth, currents, dissolved oxygen concentration of bottom waters temperature and riverine inputs, differently influence in the spatial distribution of these nutrients in the surface sediments, generating the difference between the studied coastal marine regions. These results are consistent with those described by GOMEZ (1996), which states that the fertility of the waters off northeastern Venezuela are caused by: 1) Upwelling; 2) The contributions of dissolved and particulate organic matter from the great South American rivers, particularly the Amazona and the Orinoco; 3) Coastal lagoons and other coastal water bodies that enrich the adjacent sea; 4) The local supply of nutrients from the erosion of the numerous islands and islets, headlands and cliffs on the continental shelf by internal waves. Also, ODRIOZOLA (2004) found that the Gulf of Paria and the southeaster Caribbean are under the influence of freshwater inputs. This author note that in the GP, this is a direct result of the discharge from the Orinoco River plume, whilst in the southeaster Caribbean it could be due to the discharges from both the Orinoco and the Amazon rivers, transported to the southeaster Caribbean by the Guyana Current, coinciding with those described in this study.

CONCLUSIONS

According this results can indicate that the westernmost of the PP is a substantial primary productivity zone, that can be attributed to coastal upwelling processes and the influence of the waters of the Orinoco and Amazon rivers brought by ocean currents. It was possible to distinguish two different environmental sources of organic matter and sediment for the study area. First, organic matter from marine origin in the westernmost PP, with slightly anoxic conditions thereby conserving the OM in sediment. Second, a mixture of organic matter from marine and continental with oxic conditions that not permitting its conservation, indicating the influence of the Orinoco and Amazon rivers in the GP. The differences in the distribution and content of physicochemical variables in the sediments between PP and GP is a consequence of the different geomorphology, hydrographic processes and the hydrochemical inputs from the rivers. Ocean currents and the sediment source are the most important factors that control the composition, texture and spatial distribution of the sediments and elements considered in this study.

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