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STUDY OF ANTHROPOGENICALLY INDUCED TRACE METALS ON THE CONTINENTAL SHELF IN THE SOUTHEASTERN PART OF THE GULF OF MEXICO

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ABSTRACT

A series of oceanographic cruises were perform from March 1988 to March 1990 on the continental shelf in the southeastern Gulf of México in order to study if the activities of the extraction industry of hydrocarbons are reflected in the sediments of this area. These studies made it possible to determine the area influenced by the Grijalva-Usumacinta River through granulometric (mud load) and chemical (aluminum concentration) parameters. The load sediment of the rivers moves in a northerly direction. The concentration and distribution pattern were studied in the sediments of four anthropogenically induced heavy metals: cadmium, chromium, barium and lead. Cadmium was not detected and lead values were low (18 ppm). Chromium levels were between 66 and 366 ppm and its distribution pattern suggests that this metal is transported by the rivers to the shelf area. The levels of barium concentration were between 33 and 767 ppm and its distribution pattern suggests an anthropogenic source associated to the extraction industry of hydrocarbons.

RESUMEN

Una serie de cruceros se llevaron a cabo de marzo de 1988 a marzo de 1990, en la plataforma continental del sureste del Golfo de México, con el objeto de evaluar si las actividades de explotación petrolera que se realizan en el área se reflejan de alguna manera en los sedimentos. Por medio del uso de parámetros granulométricos (contenido de lodos) y químicos (concentración de aluminio), se evaluó el área de influencia del Río Grijalva-Usumacinta y se determinó que el aporte de sedimentos de los ríos se desplaza en dirección norte. Se estudiaron los niveles de concentración y patrones de distribución de cuatro metales pesados cuyo origen se puede asociar a actividades antropogénicas: cadmio, cromo, bario y plomo. El cadmio no fue detectado y los valores observados de plomo fueron bajos (18 ppm). Los niveles medidos de cromo fueron de 66 a 366 ppm y su patrón de distribución sugiere que este metal es aportado por los ríos al área de plataformas petroleras. Los niveles de concentración del bario fueron de 33 a 767 ppm y su patrón de distribución muestra que su origen puede estar asociado con la industria de extracción petrolera.

INTRODUCTION

The Sonda of Campeche, located in the southeastern portion of the Gulf of México, is an oceanic area of high scientific and economic interest. In this area exist huge fishery resources, as well as large offshore Mexican petroleum developments. In the last few years, fixed offshore structures and thousands of miles of pipelines deliver the extracted hydrocarbons to the refineries and petroleum complex located along the coast of Veracruz and Tabasco.

The pattern of shelf-sediment transport has mainly been based on the analysis of the size of the distribution of the sediments (Shideler 1978), or indirectly determined by chemical or mineralogical means (Holmes 1982).

The sediments serve as the ultimate dump for the ocean's trace metals and provide an useful tool for the detection of important areas of past and present metal deposits. In the geochemical study of surface sediments on the southeastern portion of the Gulf of México, performed in 1988 by Rosales et al. (1992), an anomalous high barium concentration was observed, which apparently is related to anthropogenic activities associated to the petroleum industry. In the present study surface sediments were collected during the cruise Dinamo I (1990), where the research area was enlarged in comparison to previous studies. Cadmium, chromium, lead and barium were measured in the collected samples to establish the general levels of heavy metals in sediments and the areas of anomalous composition. Aluminum concentration was used to evaluate the distribution pattern of river sediments on the shelf area supported by the distribution pattern of fluvial mud (silt and clay).

STUDY AREA

The study area is located on the continental shelf of the southeastern part of the Gulf of México, between 93° 20' and 91° 00' N and 18° 30' and 20° 30' W. The Grijalva and Usumacinta Rivers and Términos Lagoon are located in the southwestern portion of the study area (Fig. 1). The shelf in the study area is wide, measuring 60 Km to the west and 140 km to the east. The coastal plain is also broad, mainly formed by low deltaic and fluvial plains as a consequence of the sediment input from the Usumacinta and Grijalva Rivers. The meridional border of Términos Lagoon presents lacustrine, lagoonal plains and marine plains can be observed on the septentrional border (Lugo-Hubp and Córdova-Fernández de Arteaga 1991).

Approximately 30 % of the fluvial discharges from México to the Gulf area are transported by the Grijalva-Usumacinta rivers (Tamayo 1990). These rivers are the principal sediment source to the sea in the area, although a net sediment outflow from Términos Lagoon through the Carmen inlet has been reported by Yáñez-Arancibia and Day (1982).

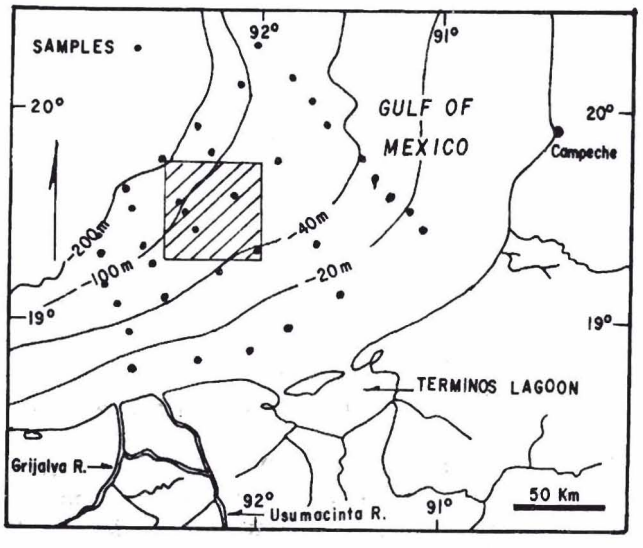

Fig. 1. Studied area (the extraction zone is shown in the square)

The climate of the area is warm and sub-humid with rainy summers (García 1973). There are three well defined climatic periods: (a) dry, from February to May, (b) rainy, from June to September and (c) windy, from October to February , with northern winds with speeds up to 50-70 knots (Yáñez-Arancibia and Day 1982). The precipitation in the area reaches 4.5 m per year.The circulation pattern of the area is mainly cyclonic (Monreal-Gómez and Salas de León 1990), with a cyclonic gyre that changes in position and intensity throughout the year.

MATERIALS AND METHODS

Surface sediment samples collected with a Smith Mc.Intire dredge on board the R/V Justo Sierra (from the National University of México) on the oceanographic cruises IMCA-I (March 3 to 13, 1988), IMCA-II (September 19 to 29, 1988), IMCA-III (March 6 to 15, 1989), and IMCA-IV (September 25 to October 7, 1989) were used to construct a compiled map which displays the distribution of the mud load coming from the Grijalva-Usumacinta Rivers. The mud content (silt and clay) was evaluated by weigh dried material passed through a 4 ø sieve (0.0625 mm).

Thirty seven samples of surface sediment collected by the same means during the oceanographic cruise DINAMO-I (March 7 to 22, 1990), on the locations shown in figure 1, were selected to evaluate aluminum, lead, chromium, cadmium, barium and carbonates.

The samples of sediment were stored in plastic bags and kept under refrigeration at 4°C until analysis. In the marine chemistry laboratory the samples were dried at 110°C and homogenized. A representative portion was taken in order to make the chemical analysis. The extraction of metals from the sediments was made by acid extraction with a mixture of water:nitric acid:fluorhidric acid:hydrochloric acid (10:5:4:1) for 30 minutes in a CEM microwave oven. Extracts were taken to 25 ml with a saturated boric acid solution and analyzed on a Varian Spectra AA-10 Plus Atomic Absorption spectrophotometer. The variation coefficient was 0.95 % for cadmium, 4.38 % for chromium, 3.93 % for lead and 1.94 % for barium; 2000 ppm of KCl was used as an internal suppressor for the determinations of aluminum and barium. The accuracy of the method was established using a sample of SD-N-1/2 sediment (IAEA 1985) and all metals reported were situated within the allowed interval of confidence at a level of significance of 0.05 %.

Carbonates were evaluated with a Bascomb's calcimeter and 4 ml 50 % hydrochloric acid was added to a sample of 0.1 g. The carbon dioxide generated is measured on a graduated column (Hesse 1971), with this method the coefficient of variation was 21.49 %. The method was standardized with pure Na_2CO_3.

RESULTS AND DISCUSSION

In order to evaluate the pattern of distribution of the sediments transported to the coastal area by the Grijalva-Usumacinta Rivers, a compilation was made of the mud content in sediment samples of the area collected during the cruises of IMCA I to IV. The distibution which could be observed (Fig. 2) shows that the load of mud sediment coming from the river apparently take a northerly direction due to currents originating in the fluvio-lagunar input.

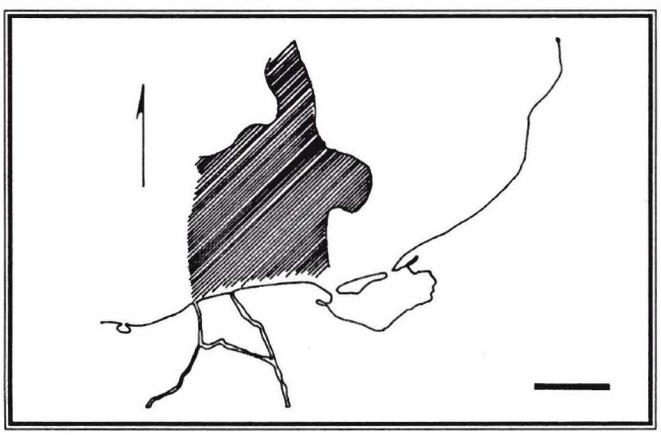

Fig. 2. Load of mud sediment [the shaded area has more than 95 % of mud (silt and clay) and scale bar covers 50 km]

Quantitatively, the most important of land derived components found in marine sediments are clay minerals and quartz (Chester 1990). As aluminum is an important component of clay minerals, aluminum concentration was measured in surface sediments of the studied area in order to evaluate, from a chemical point of view, the distribution pattern of the sediments transported by the Grijalva-Usumacinta Rivers. The values obtained are within 0.26 to 8.11 % (Fig. 3) with the highest values being near

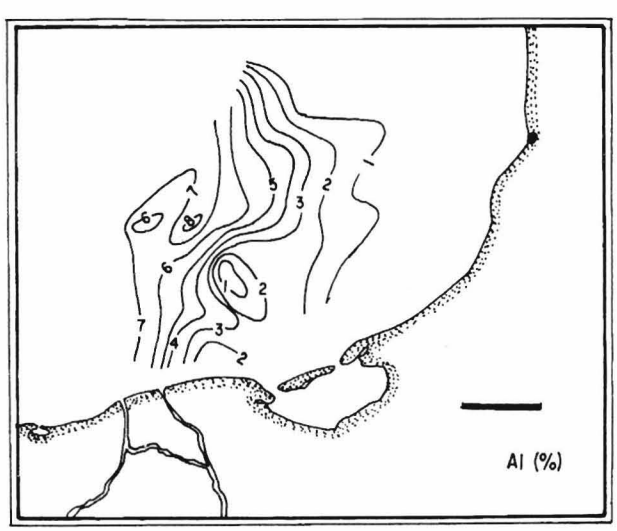

Fig. 3. Pattern of aluminum distribution (scale bar is 50 km)

the area of river discharge and with a distribution going in a northerly direction. The pattern of distribution observed is similar to the pattern found using mud content although the use of aluminum allows a more detailed analysis.

The average chemical composition of nearshore muds is: Si (25.0 %), Al (8.4 %), Fe (6.5 %), Na (4.0 %), Ca (2.9 %), K (2.5 %) and Mg (2.1 %) (Chester 1990), but as nearshore sediments are deposited under a wide variety of conditions and are strongly influenced by the adjacent land masses, their chemical composition is highly variable. The most important factors controlling the condition under which recent sediments are deposited are: i) the rate of sediment supply, ii) the tide level and iii) the intensity or persistance of local water movements which rework the unconsolidated material and supply new material (Calvert 1976).

The sediments of the southeastern part of the Gulf of México are formed essentially by a two component (clay and carbonate) system. According to carbonate concentration a transitional region was observed across the mouth of Términos Lagoon, with carbonate values lower than 50 % to the west and higher than 50 % to the east (Carranza-Edwards *et al.* 1993).

Four heavy metals (Ba, Cr, Cd, Pb), usually introduced anthropogenically to the natural environment, were studied. Cadmium contents were below the analytical detection limit (0.034 ppm). Lead contents were within normal levels (18 ppm) and with no great variations. The levels of concentration and pattern of distribution for chromium and barium will therefore be discussed in more detail.

Chromium is an element present in many minerals in the crust of the earth. It is considered to be an essential part of living organisms. However, over the past several decades increased quantities of chromium compounds have been used by man and introduced into the environment.

Generally chromium is found in soils in concentration of 10 to 90 ppm (Merian 1991). In nearshore areas it may vary considerably as it can be seen in Table I. Data on Mexican coastal sediments show the highest values in Laguna del Ostión (210 ppm) and Laguna de Alvarado (175 ppm) in the State of Veracruz (Villanueva and Botello 1992). A maximum concentration of 100 ppm of chromium in agricultural soil has been recommended. In Switzerland a threshold value has been fixed at 75 mg Cr/Kg for agricultural soils and in Germany at 100 mg Cr/Kg (Merian 1991).

In the present investigation, a range from 83 to 316 ppm of chromium, with an average value of 166 ppm was observed. The pattern of distribution for chromium (Fig. 4) suggests that this metal is supplied by the river, which, in this case, would resemble the pattern of distribution for aluminum.

Barium concentration is a good diagnostic anthropogenic tracer. Barite ($BaSO_4$) is used extensively in mud drilling and is introduced to shelf sediments during the process of exploration and exploitation of hydrocarbons. Barite is a very fine compound with a high specific gravity

TABLE I. HEAVY METAL CONCENTRATION (ppm) IN DIFFERENT NEARSHORE AREAS

Metal	Gulf of Paria*	Massachusetts*	Oregon Cont. Shelf*	This work
Ba	301-394	310	661	33-767
Cr	31-93	33	191	66-366
Pb	13-22	25	10	18

* Calvert 1973

and with a hydraulic equivalent of fine sand or coarse silt. Thus the movement of this substance reflects coarse granular material and not fine silts and clays (Holmes 1982).

In the present investigation an interval from 33 to 767 ppm of Ba with an average of 147 ppm was observed in the study area. The pattern of distribution of barium observed (Fig. 5) in the area may be related to the exploitation of hydrocarbons, given that the maximum values observed were found adjacent to the exploitation area (Fig. 1).

The concentration of barium in shelf areas vary considerably as reflected in Table I. In the northwestern part of the Gulf of México, Holmes (1982) found barium concentrated in four areas with values greater than 200 ppm. Three of these areas were directly adjacent to major oil fields on the inner shelf, the fourth is in the sea directly in front of the Río Grande. In this case, the tongue of this Ba-rich sediment is a monitor of the sediment transported from the mouth of the Matagorda Bay and the northern region.

CONCLUSIONS

Mud content in sediments of the area studied shows the degree of fluvial supply and that pattern of distribution may be related to the influence of currents.

The pattern of aluminum distribution agrees with the distribution based on mud sediments. It allows a better definition of the area of river discharge on the basis of higher aluminum concentration.

Cadmium was not detected in the area studied. Lead showed a homogeneous distribution with low concentration values (18 ppm).

Values detected for chromium were on the 83 to 316 ppm interval, with an average value of 193 ppm. The distribution pattern obtained suggests that chromium concentration in the area is mainly due to the contribution of the Grijalva-Usumacinta Rivers.

Barium concentration values evaluated were on the 33 to 767 ppm interval, with the highest values located in the area where activities of hydrocarbon extraction occur.

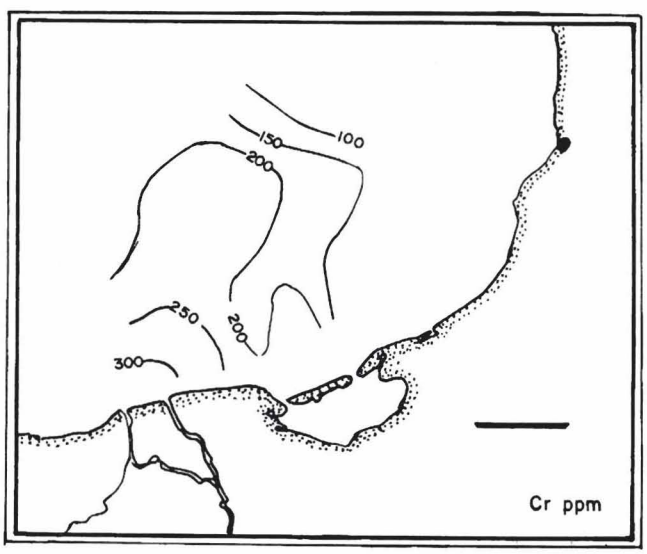

Fig. 4. Pattern of chromium distribution in bottom sediments (scale bar covers 50 km)

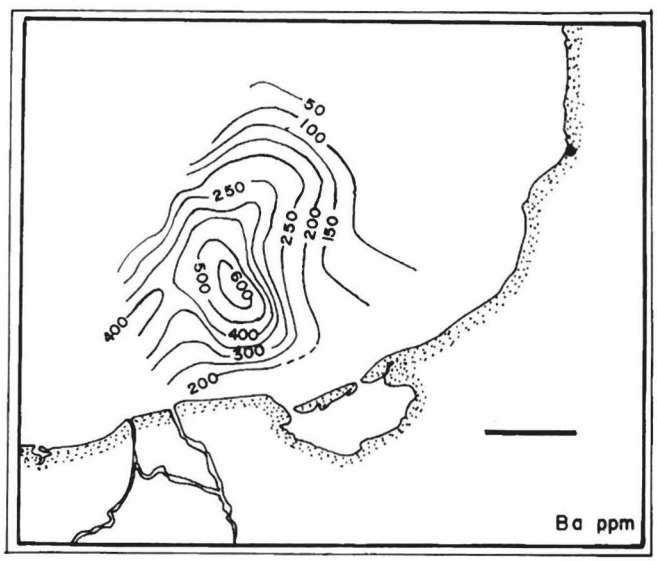

Fig. 5. Pattern of barium distribution in bottom sediments (scale bar covers 50 km)

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