METALS DISTRIBUTION AND CONTAMINATION IN THE GULF OF MEXICO

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INTRODUCTION

Metals are a natural part of the earth's crust and are found in rocks, soils, sediments, water and volcanic eruptions. However, in the years following the industrial revolution major changes occurred in the natural concentration of metals, due to their widespread use for industrial and human purposes.

One clear example of this is found in the Gulf of Mexico, where the excessive presence of some metals in the coastal ecosystems is a result of their introduction through contamination processes and contribution by rivers, which include the two largest deltas that run into the Gulf of Mexico: the Mississippi River in the U.S.A. and the Grijalva-Usumacinta rivers in Mexico.

The contamination from the rivers and deltas includes toxic wastes such as metals, oil-based hydrocarbons and persistent organic contaminants such as pesticides and PCB. The industrial and commercial activities carried out in the big port areas of Brownsville, Corpus Christi, Houston and Galveston in the U.S.A., and Tampico-Madero, Altamira, Veracruz, Alvarado, Coatzacoalcos, Dos Bocas and Ciudad del Carmen in Mexico, are potential sources of contamination to marine and coastal environments.

There are 22 rivers in Mexico that run into the Gulf, the most important of which is the Rio Grande (Río Bravo), that forms part of the border between Mexico and the U.S.A. A series of dams have been built along the Rio Grande, regulating its flow into the Gulf of Mexico. The second most important river is the Río Usumacinta, which has a basin only slightly smaller than that of the Río Panuco, but has higher drainage due to its localization in a tropical zone.

It has been calculated that approximately 95% of the metals transported by rivers are removed and deposited on the ocean margins such as estuaries, the continental shelf and the continental slope. Studies conducted more than 20 years ago on the Gulf of Mexico coast have demonstrated the presence of high concentrations of toxic metals such as Pb, Cd, Cr and Ni. The results show that the worst metal contamination problems are found in semi-enclosed water bodies, and particularly in bays, estuaries and coastal lagoons. In these areas metals are available in high concentrations, depending on the nature and type of sediment and the physical and chemical characteristics of the water.

In order to understand the behavior and geochemical balance of metals, it is necessary to study their chemical nature, residence time, solubility, movement, bioavailability, transfer to sediments, interaction between the aqueous and the sedimentary phases, biomagnification at different trophic levels and, most importantly, their toxicity. These studies will allow the identification of the effects and disturbances that metals can cause in the biota and their damage to human health.

SOURCES OF METALS

The majority of the metals that are used in industrial activities are present in the coastal regions of the Gulf of Mexico, particularly in the vicinity of oil refineries, fertilizer plants, mining and metal industries, and also around the coastal cities with large populations. Oil drilling activities also use large quantities of drilling fluids that contain metals such as chromium and barium. Similarly, the discharge of untreated domestic waste generates large volumes of sludge enriched with metals such as Pb, Zn, Cd and Cr, which are discharged into rivers or directly into the sea. Metals are also introduced into marine and coastal environments by runoff from soils, erosion of rocks, volcanic eruptions, use of fertilizers and pesticides in agricultural zones, and waste from foundries and chrome plating plants.

Studies undertaken on the last 50 kilometers of the Coatzacoalcos River showed variable content of suspended matter throughout the year. The highest values occur in August, which coincides with the rainy season, averaging 99.7 mg L^{-1} for bottom water (Bahena *et al*. 2002). The highest average content of dissolved metals occurred in April, with 42 mg L^{-1} of Zn and 6.0 mg L^{-1} of Cu in surface water, and 4.3 mg L^{-1} of Cr in bottom water. In this case the concentration of dissolved metals is apparently a function of the river's flow and anthropogenic discharges in the area.

The concentration of suspended matter in eight rivers that run through the USA and which flow into the Gulf of Mexico ranged from 12 and 954 mg L^{-1}. The concentration of metals in the suspended matter is a function of the type of material, and a correlation between dissolved metals and metal content in the suspended matter was not observed (Turekian and Scott 1967). Table 22.1 presents the percentage of some metals transported in association with suspended matter in some rivers that flow into the Gulf of Mexico, according to Páez *et al*. (1987).

The majority of metals is insoluble in water at neutral or basic pH values, but is easily adsorbed by particulate matter or sediments, which are their final destination, where their concentration is up to 10^3 to 10^7 times higher than in the water column. The metals associated to the sediment are assimilated by benthic organisms or form ionic complexes with water-soluble anions. Therefore, the analysis of metals in suspended particles, sediments and organisms provides information on their source, routes, fate and effects, as well as their possible environmental risk.

One of the main characteristics of the metals found in coastal ecosystems is that organisms can store large concentrations of a given metal (bioaccumulation), and this consequently leads to an increase in metals concentrations in the upper trophic levels (biomagnification). Therefore, benthic organisms are the most affected by contamination with toxic metals, such as Hg, Pb, Cr and Cd in ocean and coastal zones, which drastically reduces their ability to survive and, sometimes, leads to their complete disappearance.

Table 22.1. Concentration of each metal transported by suspended matter in some rivers of Gulf of Mexico.

River	Fe	Mn	Cu	Cd	Co	Pb
Palizada	99.6	95.8	64.6	19.7	13.6	74.2
Candelaria	87.9	89.7	25.0	22.3	10.0	18.2
Cruces	90.8	40.0	38.7	53.8	89.0	81.0
Pinas	96.8	78.3	8.7	36.0	53.3	37.8
Mississippi	99.0	98.0	90.0	83.0	97.6	-

METAL LEVELS IN COASTAL SYSTEMS OF THE GULF OF MEXICO

The growing contamination of the coastal and marine areas is becoming a major threat in Mexico. This is why some institutions are undertaking studies that have the objective of evaluating the level and behavior of metals in water and sediments, particularly on the coast of the Gulf of Mexico.

WATER

Research on dissolved/particulate metals of coastal areas of the Gulf of Mexico is scarce, due to the difficulty in quantifying their content, distribution and behavior in water (Villanueva and Botello 1998).

SEDIMENTS

Cadmium

The data presented in this review shows that the average of total Cd in the sediments of seven coastal systems of the state of Veracruz (Álvarez *et al*. 1986; Páez *et al.* 1986; Rodríguez 1994; González 1995) (Fig. 22.1), and 14 in the state of Tabasco (Botello 1996) is high, mainly in cores from the Laguna El Yucateco (5.18 µg g^{-1}) and Laguna Limon (3.22 µg g^{-1}) (Fig. 22.2). As can be seen in Figures. 22.1 and 22.2, all the lagoons and rivers of the states of Veracruz and Tabasco contain Cd levels above the minimum concentration that causes adverse biological effects to aquatic organisms (ERL 1.2 µg g^{-1}) (Long *et al*. 1995).

Although the data on the total concentration of metals is very useful, it is not sufficient for the evaluation of their transport and residence time in sediments. This is because part of the total metal content is found in solid particles and minerals, and part is bioavailable and incorporated into the sediment, either by precipitation, flocculation or adsorption (Loring 1979). The latter represents the metals that were initially weathered in discharges of anthropogenic origin, and another part derives from ions released when diagenetic conditions are disturbed. As a consequence this fraction is available for accumulation in the aquatic biota (Luoma and Jenne 1976; Loring 1979).

The concentration intervals of total Cd vary from 1.09 µg g^{-1} in Laguna Mandinga to 2.18 µg g^{-1} in the Río Coatzacoalcos, and 2.2 µg g^{-1} in Laguna Salada; for the bioavailable fraction the levels vary from 0.22 µg g^{-1} in the Río Blanco to 1.37 µg g^{-1} in Laguna Sontecomapan (Fig. 22.1). All of these areas are located in the state of Veracruz.

The presence of Cd in the sediments of the coastal lagoons of Veracruz is considered a normal component of the marine sediments and of the phosphoric rocks, whereas the high values detected in the Laguna El Yucateco and Laguna Limon (both in Tabasco) are directly related to urban discharges, the sedimentary characteristics and organic matter content of the sediment which forms organic complexes with Cd, as well as industrial wastes in these areas.

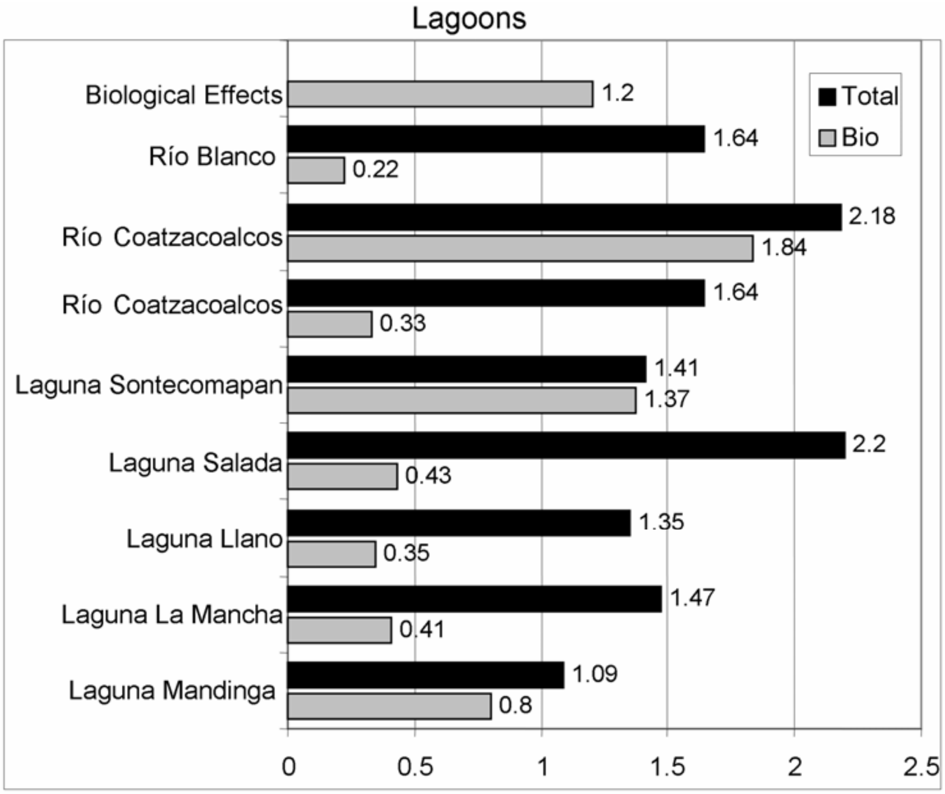

Fig. 22.1. Concentrations of cadmium (µg g^{-1}) in sediments of the coastal systems of the state of Veracruz.

Lead

The highest concentrations of total Pb in the coastal systems of the state of Veracruz have been recorded in Laguna del Llano (77.2 µg g^{-1}), Laguna Salada (78.8 µg g^{-1}) and Laguna La Mancha (81.1 µg g), near the Laguna Verde nuclear power plant (Rodríguez 1994). Laguna Sontecomapan (González 1995), and Río Coatzacoalcos (Villanueva and Botello 1998) and Río Blanco Álvarez *et al*. 1986) exhibit levels below the effects range-low (ERL) of 46.6 µg g^{-1} proposed by Long *et al*. (1995), in which case adverse effects on organisms' tissues are not expected.

The above-mentioned lagoons also exhibited the highest values of bioavailable Pb (between 11.6 µg g^{-1}and 21.4 µg g^{-1}) (Fig. 22.3). This indicates that the organisms, mainly bivalve molluscs, are exposed to severe Pb accumulation in these lagoons.

The highest registered value of Pb (Fig. 22.4) is found in Laguna de las Ilusiones (Tabasco), with 158.7 µg g^{-1} (Valencia 1989), and in Laguna El Yucateco (117 µg g^{-1}) (Botello 1996). These values are directly related to the constant, and occasionally massive, input of wastewater. They are also related to the atmospheric emissions from urban and industrial areas from the city of Villahermosa, which are transported to other regions of the Gulf of Mexico because Pb is volatile and tends to get deposited in areas other than its place of origin, depending on the predominant wind patterns in the Gulf of Mexico (Valencia 1989).

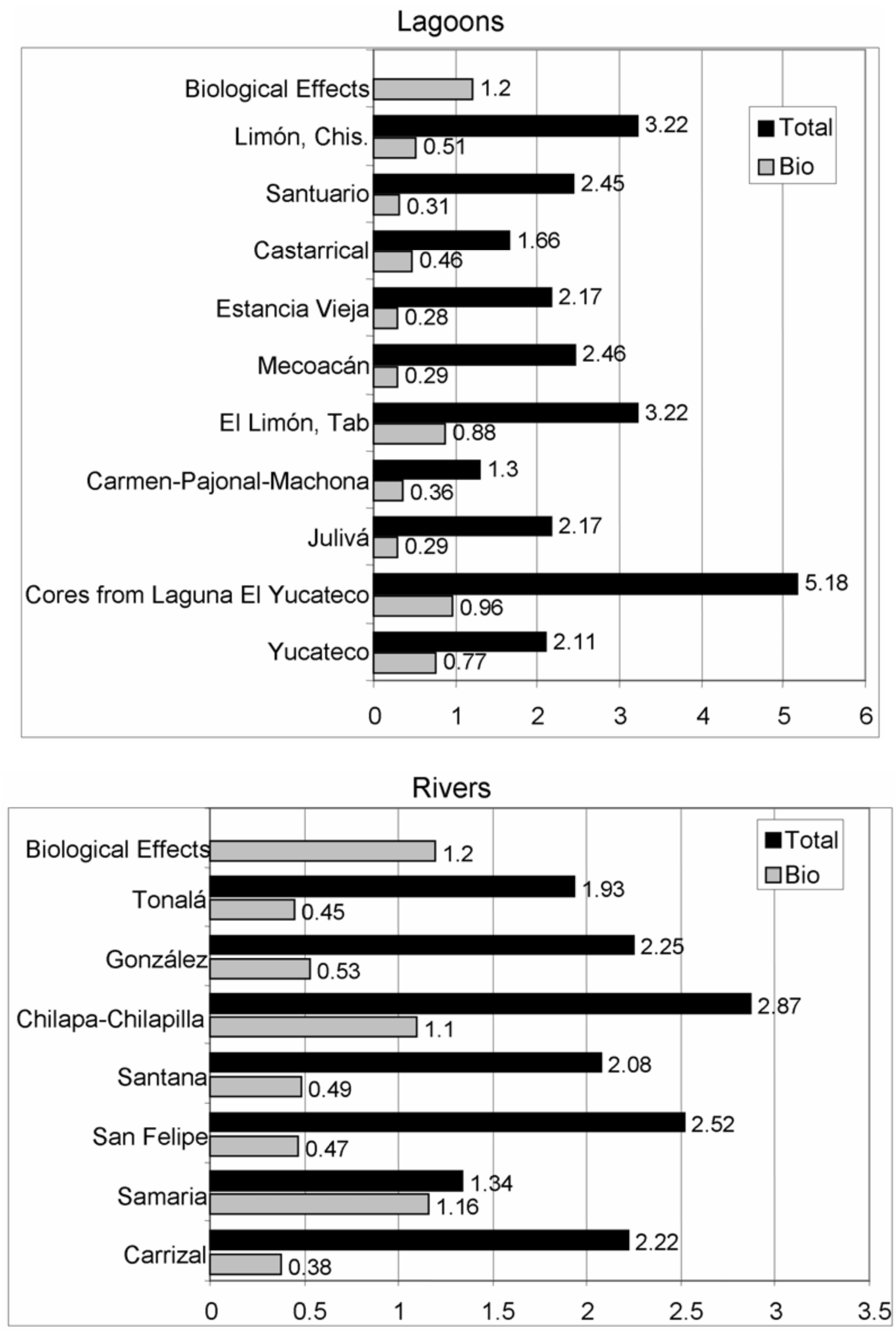

Fig. 22.2. Concentrations of cadmium ($\mu g\ g^{-1}$) in coastal sediments of the state of Tabasco.

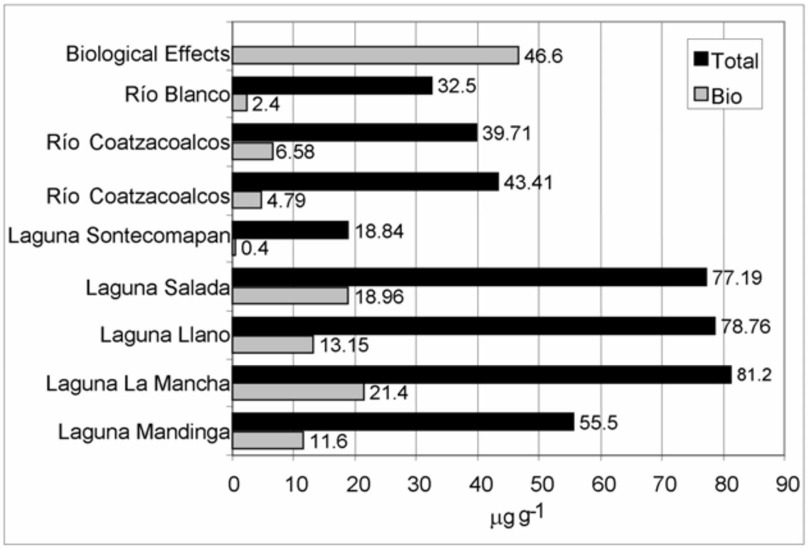

Fig. 22.3. Concentrations of lead (µg g^{-1}) in coastal sediments of the state of Veracruz.

The same phenomenon has been registered in the area of the Río Coatzacoalcos where Pb is dispersed into the river as PbO and $(CH_3CH_2)_4Pb$ because it is used as a sub-product in the production of anti-detonants. The factory's effluent is deposited in a settling tank where the metal is recovered with the solids, and the liquid waste is sent to the Río Coatzacoalcos by an underwater outfall. The Pb discharge through the outfall is intermittent, resulting in continuous metal accumulation (Ochoa *et al*. 1973).

The Pb concentrations in these systems are up to 150% above the ERL value (46.6 µg g^{-1}) established by Long *et al*. (1995), which is the level above which adverse effects on organisms may be observed (Figs 22.3 and 22.4).

Chromium

Laguna del Ostión (140.7 µg g^{-1}) (Villanueva and Botello 1992) and Laguna Alvarado (159.7 µg g^{-1}) (Rosales *et al*. 1986), both in the state of Veracruz, and Laguna El Limon (249 µg g^{-1}) and Laguna Juliva (223 µg g^{-1}) in Tabasco register the highest levels of Cr in sediments in these states (Fig. 22.5). These values exceed the ERL (81µg g^{-1}) established by Long *et al*. (1995) by up to one order of magnitude.

These data suggest the existence of discharges from nearby industries to these locations, mainly tanneries and fertilizer plants that discharge waste products in the form of chromates. Cr is a metal that tends to accumulate in sediments, which contributes significantly to its increased level in these areas. However, these high values are contrasted with the bioavailable fractions, which are lower than 5.5 µg g^{-1} for all areas where information was available.

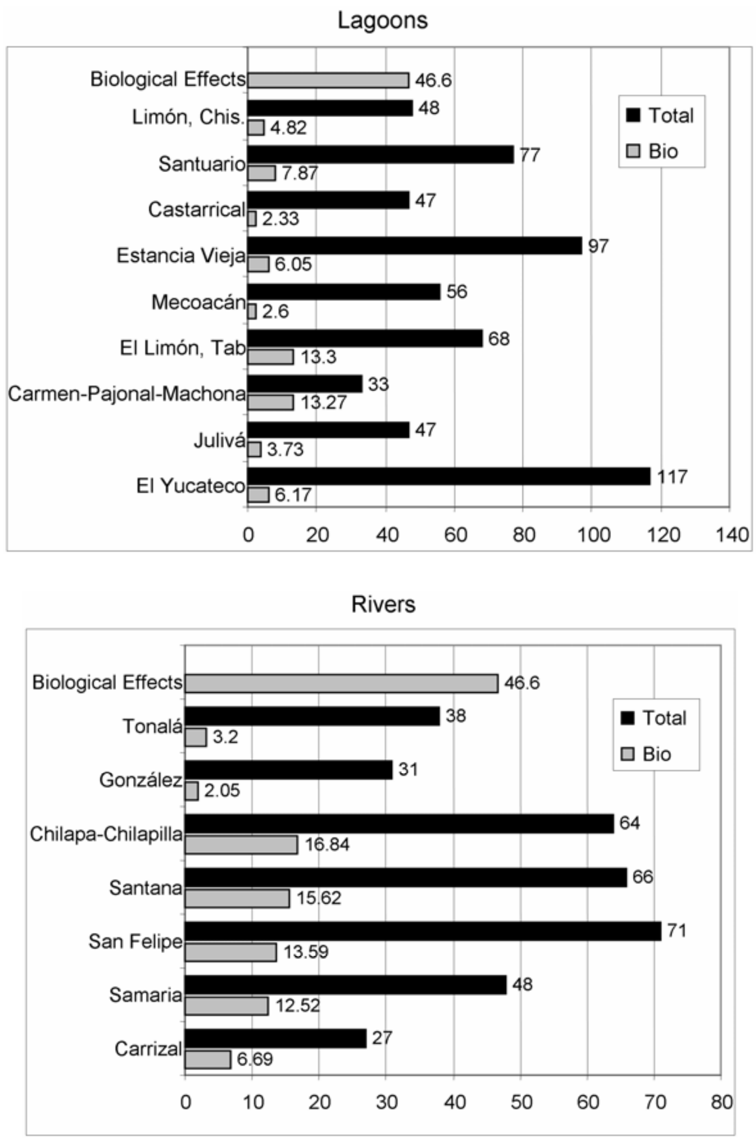

Fig. 22.4. Concentrations of lead (µg g^{-1}) in coastal sediments of the state of Tabasco.

Nickel

The presence of Ni in sediments of the coastal zones of the Gulf of Mexico has a relatively uniform pattern, ranging from 26.29 µg g^{-1} (Laguna Mandinga) to 98.40 µg g^{-1} (Río Tonala) (Villanueva and Botello 1992), followed by the Jamapa, Actopan, and Papaloapan rivers in the state of Veracruz, with concentrations no greater than 100 µg g^{-1} (Vázquez *et al.* 1995). The bioavailable concentrations are uniform for the lagoons in the state of Veracruz (<5.0 µg g^{-1}). In contrast, El Limon (141 µg g^{-1}) and Juliva (139 µg g^{-1}) lagoons, and the Río Chilapa-Chilapilla (155 µg g^{-1}) in Tabasco, are up to one order of magnitude above the ERL value (20.9 µg g^{-1}) established by Long *et al*. (1995) (Figs. 22.6 and 22.7). The reported values for the Río

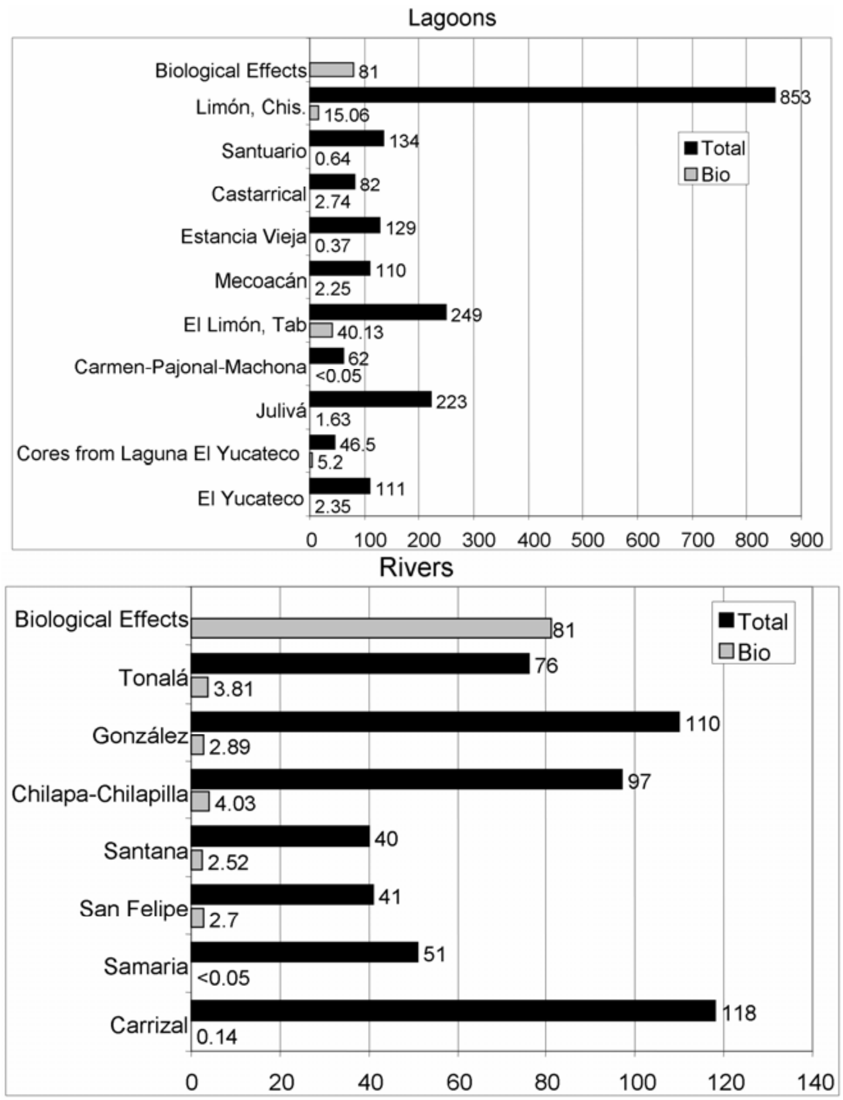

Fig. 22.5. Concentrations of chromium ($\mu g\ g^{-1}$) in sediments of coastal systems of the state of Tabasco.

Tonala suggest that this metal, in conjunction with vanadium, forms part of the composition for crude oil, and Ni is also used as a catalyzing agent in petroleum refining processes. Therefore, it is assumed that these concentrations are directly related to the petrochemical industries in the area, such as La Venta, El Panal and Cinco Presidentes in the state of Tabasco. These plants have been in operation for several decades and their effluents have always been discharged directly into the river without any previous treatment (Villanueva and Botello 1992).

ORGANISMS

Large scale monitoring programs have been implemented, starting with mussels, to evaluate the presence of potentially toxic elements and other contaminants in marine environments (Goldberg *et al.* 1978; Lauenstein *et al.* 1990). Although mussels are

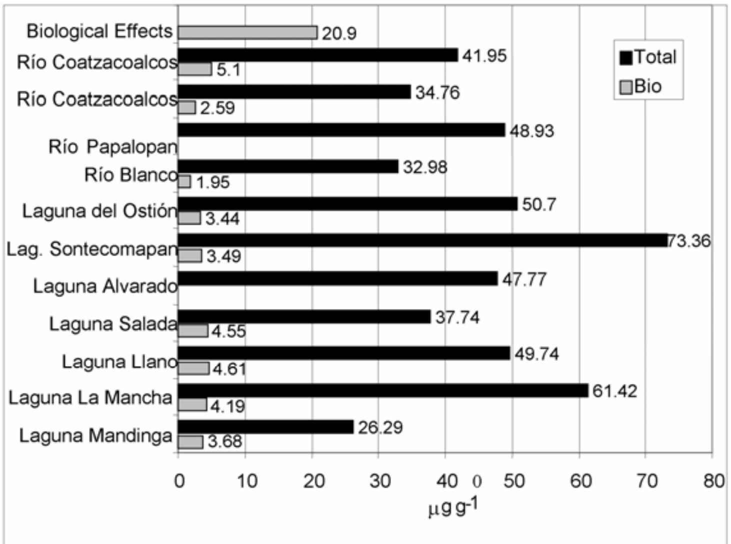

Fig. 22.6. Concentrations of nickel (µg g^{-1}) in sediments of coastal systems of the state of Veracruz.

recommended as an alternative for the analysis of water and sediments, there are additional variables that need to be investigated (Phillips 1977; Westerhagen *et al.* 1978; Páez *et al.* 1987; Villanueva and Botello 1998).

Information on trace metals accumulation in mussels has been collected since the 1970s through the Mussel Watch Program, which has been analyzing concentrations of Cd, Cu, Ni, Ag and Zn in bivalve molluscs of the northern coast of the Gulf of Mexico, corresponding to the U.S.A. (Goldberg *et al.* 1978; Lauenstein *et al.* 1990). Table 22.2 shows the results of two decades of research in this program. Based on these results Lauenstein *et al.* (1990) conclude that the concentration of Pb, Cd, Cu, and to a lesser extent Zn, in bivalve molluscs has decreased during the last decade. The authors do not offer a definitive answer regarding the behavior of these metals but they propose that the increase in Cu in the environment is inversely proportional to the concentration in the molluscs, mainly due to the physiological processes of these organisms.

Lead

The levels of Pb in *Crassostrea virginica* exhibit an heterogeneous pattern throughout the Gulf of Mexico coast, and register the highest values in Laguna Mandinga (11.55 µg g^{-1}) (Hernandez *et al*. 1996). The bioavailable concentrations of Pb in this lagoon were the highest registered for the Gulf of Mexico. The San Andres (5.85 µg g^{-1}; Vázquez *et al.* 1990), La Mancha (3.24 µg g^{-1}; Rodríguez 1994) and Carmen (3.04 µg g^{-1}) lagoons register values above the permitted limit for human consumption, which is 2.5 µg g^{-1} (Nauen 1983) (Table 22.3).

There is no doubt that these results reflect the increase in human and industrial activities in the area, and the concentration and distribution of the metals are influenced by the direction of coastal winds and currents that carry them from the cities and coastal industries of Tampico, Veracruz and Tabasco. The high level registered in Laguna Mandinga reflects the direct disposal of Pb-enriched waste, which probably originates in the industrial areas of Cordoba and Orizaba

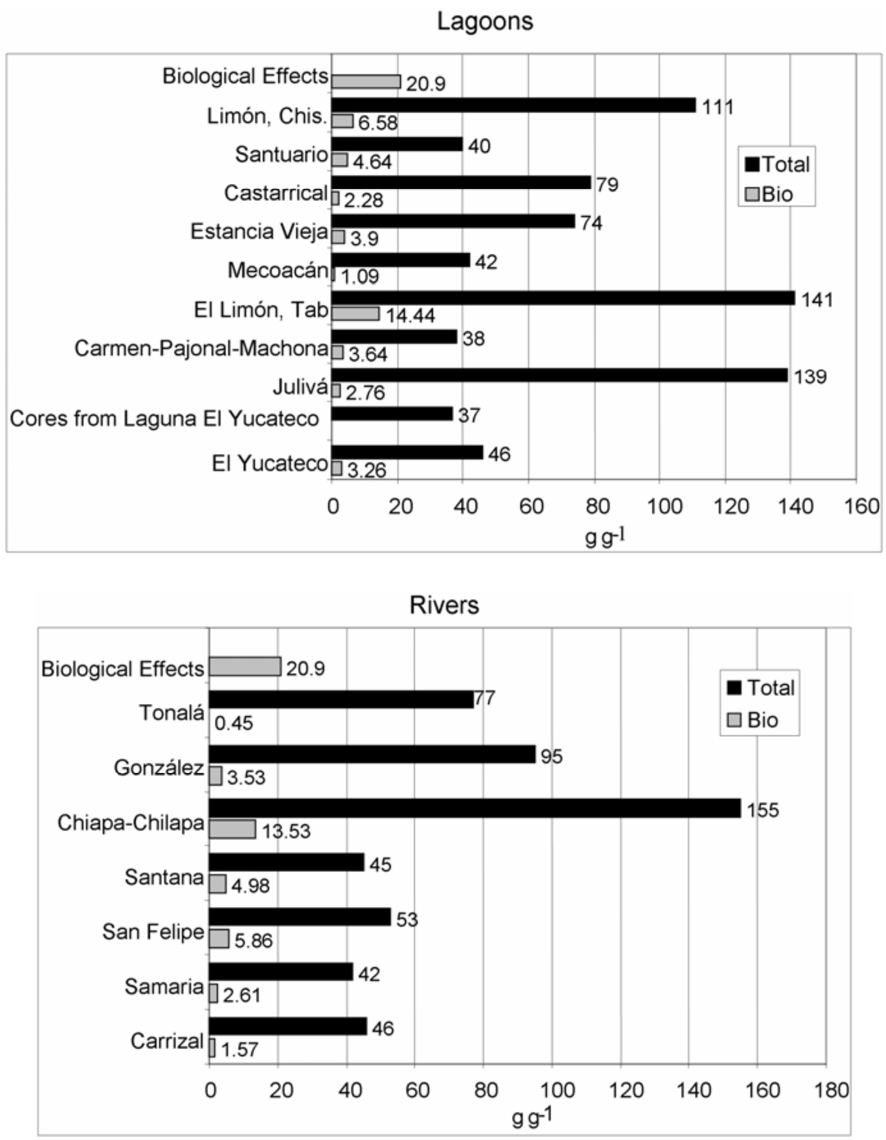

Fig. 22.7. Concentrations of nickel (μg g^{-1}) in sediments of coastal systems of the state of Tabasco.

and is then transported to the coastal zone by the Blanco and Jamapa rivers in Veracruz.

Pérez *et al*. (1984) analyzed two species of fish, *Centropomus undecimalis* and *Euguerres* sp., and reported the highest values of Pb for Gulf of Mexico organisms in the skull and kidney of these fish, reaching 50.00 μg g^{-1}.

Despite the high level of industrialization and urbanization of the state of Veracruz, the average concentration of Pb in *C. virginica* (4.38 $μg^{-1}$) is similar to that in the state of Campeche (4.59 μg g^{-1}), which, in turn, is lower than concentrations reported for the state of Tamaulipas (5.85 μg g^{-1}).

Table 22.2. Interval and average concentrations (μg g^{-1} dry weight) of metals in mussels of 13 sites on the northern coast of the Gulf of Mexico (Mussel Watch Program 1976-1978 and 1986).

	1970s			1980s		
Element	Range		Average	Range		Average
Ag	0.69	3.20	1.81	0.60	4.50	3.02
Cd	2.10	9.10	4.49	1.40	7.00	3.95
Cu	90.0	200	157.6	45.0	190	118
Ni	1.70	4.50	2.52	1.20	2.40	1.68
Pb	0.27	1.10	0.68	0.30	0.86	0.43
Zn	520	5100	1618	560	3500	1446

Table 22.3. Average values of metals in *Crassostrea virginica* (μg g^{-1} dry weight) in coastal lagoons of the Gulf of Mexico (Nauen 1983).

State	Cd	Cr	Pb	Ni	Reference
Tamaulipas					
San Andres	2.55		5.85	3.40	Vazquez *et al*. (1990)
Veracruz					
Mandinga	3.13	3.32	11.55	5.77	Hernandez *et al*. (1996)
La Mancha	1.34	5.13	3.24	2.88	Rodriguez (1994)
Llano	1.11	4.58	2.23	4.13	Rodriguez (1994)
Tabasco					
Carmen	3.29	6.31	51.80		Botello (1996)
Machona	2.94	5.17	22.38		Botello (1996)
Mecoacán	1.08	6.47	4.08		Botello (1996)
MALSC[a]	0.20	1.00	2.50		

[a] Maximum Allowable Limit for Seafood Consumption.

Table 22.4. Metal concentrations in fish and crustacean tissue (μg g^{-1} dry weight) in Laguna El Yucateco, Tabasco (Botello 1996).

Species	Common Name	Cd	Cr	Pb	Ni
Cichlasoma friedrichsthali	Yellowjacket cichlid	0.61	1.24	15.68	4.99
Megalops atlanticus	Tarpon	0.43	1.03	10.06	4.10
Cichlasoma bifasciatum	Twoband cichlid	0.36	2.10	5.29	4.57
Cichlasoma urophthalmus	Mexican mojarra	0.39	0.16	8.89	5.74
Callinectes rathbunae	Crab	0.71	1.26	12.13	8.75
MALSC[a]		0.20	1.00	2.50	-

[a] Maximum Allowable Limit for Seafood Consumption

Botello (1996) undertook a study of metals in several species of fish of Laguna El Yucateco, Tabasco, and reported that Pb concentrations in the yellowjacket cichlid *Cichlasoma friedrichsthali* (15.68 μg g^{-1}) are higher than for any other species including the four species shown in Table 22.4, and are above the maximum permitted level for the human consumption of aquatic food according to Nauen (1983) (2.50 μg g^{-1}).

Cadmium and Chromium

Table 22.3 shows the highest concentrations measured in *C. virginica* from Laguna del Carmen (3.20 μg g^{-1}; Botello 1996), Laguna de Términos (5.33 μg g^{-1} and 4.17 μg g^{-1}; Hicks 1976; Vázquez *et al.* 1993) and Laguna Mandinga (3.13 μg g^{-1}; Hernández *et al*. 1996). These values exceed the permissible limit for human consumption (2.0 μg g^{-1}). The high concentrations in Laguna del Carmen and Laguna de Términos are due to the discharge of wastes from the Panuco and Palizada rivers, and the contribution of industrial and nearby agricultural activities. There is clearly a general association between densely urbanized areas and the proximity of areas with mining operations, electro plastic and petroleum processing activities. By contrast, the concentrations reported in fish from Laguna El Yucateco are between 0.36 μg g^{-1} and 0.71 μg g^{-1} (Table 22.4). The concentrations of Cr measured in the oyster *C. virginica* are high for all the areas reported in Table 22.3, relative to the maximum permitted limit of 1.0 μg g^{-1} (Nauen 1983), which demonstrates the high availability and accumulation of this metal from sediment to these bivalve molluscs. The concentrations in analyzed fish from Laguna El Yucateco are slightly higher than the maximum permitted limit for human consumption of aquatic food, which is 1.0 μg g^{-1} (Table 22.4).

Nickel

Although nickel is an essential metal for living organisms, it is the metal with least tendency for bioaccumulation, and significant levels of Ni were only measured in molluscs from Laguna del Ostió in Veracruz (84.00 μg g^{-1}; Villanueva *et al.* 1988). However, this concentration is not very high when compared to the value reported by Segar (1971) in the gastropod *Crepidula fornicata* (850 µg g^{-1}), which did not have a toxic effect to the organism. The levels reported by Villanueva *et al.* (1988) for *Diaptherus olisthostomus* (78.00 µg g^{-1}) are high relative to other data, e.g., those reported by Izaguirre *et al.* (1992) for *Mugil curema* (10.30 µg g^{-1}) on the Mexican northeastern Pacific (Table 22.3).

The concentrations shown in Tables 22.2 and 22.3 for the oyster *C. virginica* and five different species of fish are very similar, ranging from 2.88 µg g^{-1} in oysters from Laguna Mandinga to 8.75 µg g^{-1} in crabs from Laguna El Yucateco.

Núñez (1996) analyzed ten metals in six different organs of the sharks *Carcharhinus limbatus* and *Rhizoprionodon terraenovae* in the Gulf of Mexico (Table 22.5), taking into account the size, age and sex of these species. The study established the risk factor for consumption according to the measured concentrations of metals, particularly those that are highly toxic, such as As, Cd, Hg and Pb. These shark species represent an important part of the fisheries at national level.

Unlike other chemicals such as pesticides and artificial radioisotopes, metals constitute an essential part of living beings. The adverse effects of metals depend on their interaction with the organism or with the whole community. There is a delicate balance between organisms and their environment, which is determined by the use of certain metals in catalytic processes within cells and their bioaccumulation at toxic levels. This balance is influenced not only by the abundance and availability of metals in the Earth's crust, but also by the transformations that they undergo as a consequence of physical, chemical and biological changes that are provoked and/or accelerated by human activity (Páez 1996).

The majority of the metals is insoluble in water with neutral or basic pH, but is easily taken up by particulate material, such as organic matter or sediments. These are the final destination of metals in the aquatic environment, where the concentrations are from 10^3 and 10^7 times higher than in the water column and where they can be assimilated by organisms or form ionic compounds with water-soluble anions. Therefore, in the oceans and coasts the benthic organisms are the most affected by the concentrations of toxic metals, due to their direct interaction with the sediments (Laws 1993).

The following considerations can be made on the reported results on the high concentrations of toxic metals in sediments and organisms in the coastal systems of the Gulf of Mexico: the contamination by Pb seems to be a phenomenon limited to the critical area of rivers, where there are considerably degraded and completely destroyed regions; the variation in the concentration of Pb in sediments depends on the behavior of industrial discharges, the tendency of Pb to accumulate, the intrinsic characteristics of the sediment which can sustain bacterial populations that allow the incorporation of Pb through their metabolic activity, and the affinity with organic matter (Landner 1970; Hartung and Sinman 1972).

The high concentrations of bioavailable Pb in certain coastal environments of the Gulf of Mexico can be attributed to the following: a) the association between the metal and organic matter, and their precipitation as Pb carbonates; b) the Pb is not completely available to the organisms; c) the Pb compounds are soluble in water; d) the periodicity of Pb discharges; e) the magnitude of the Pb discharges; f) the flow of the river or lagoon, as well as the influence of the tides, and above all the organic compounds with Pb contained in gasoline, since Hg and Pb are two metals that are discharged intermittently in the Coatzacoalcos River zone (Ochoa *et al*. 1973; Páez *et al*. 1986).

Table 22.5. Concentration of toxic metals in different species of sharks in the Gulf of Mexico.

Metal	As	Cd	Hg	Pb
Maximum allowable consumption[a]	0.05 mg/kg/day	0.008 mg/kg/week	0.03 mg/kg/day	2.50 mg/kg/day
Concentration detected in *C. limbatus*	3.15 mg/kg	0.30 mg/kg	3.01 mg/kg	1.79 mg/kg
Concentration detected in *R. terraenovae*	3.68 mg/kg	0.40 mg/kg	0.75 mg/kg	3.35 mg/kg
Maximum allowable consumption[b] of meat of *C. limbatus*[a]	1.11 kg/day	1.86 kg/week	0.0697 kg/day	97.76 kg/day
Maximum allowable consumption[b] of meat of *R. terraenova*[a]	0.951 kg/day	1.40 kg/week	0.287 kg/day	52.23 kg/day

[a] According to limits established by FAO/OMS
[b] Considered for an adult person with 70 kg weight

The levels of metals in the sediments of coastal areas of the Gulf of Mexico are several orders of magnitude higher than those measured in the water column of coastal areas and the open sea. The concentration and distribution of Pb, Cd and Cr in sediments are in a similar range to those of coastal zones with no impact, with some exceptions.

The behavior of metals in organisms depends on several factors, such as their absorption, excretion, storage, and the efficiency of their regulation or detoxication system (Bryan 1971). Therefore, the physiological and biochemical strategies can vary from one species to another (Gerlach 1981), which leads to variable concentrations among species, organisms, tissues, as well with age, sexual maturity, feeding habits, migration, dynamics, metabolism, and mainly in relation to the different affinity of the metals with specific organs (Hicks 1976; McFarlane and Franzin 1980).

METALS ON THE CONTINENTAL SHELF OF THE GULF OF MEXICO

The Gulf of Mexico is an open basin with a well-developed continental shelf. It receives a significant supply of several terrigenous materials. The area of the continental shelf has little topography, with predominance of depositional factors over structural ones.

CONTINENTAL SHELF ORGANISMS

Vázquez *et al*. (2001) undertook studies of metals (Cu, Pb, Cd, Cr, Mn, Zn, Ag, Ba and Fe) in fish and shrimp that were collected in different areas of the Campeche Bay. They showed that the concentration of these metals in muscles, gonads and viscera (Cu: 1.3-10.5, Pb: 0.15-8.5, Cd: 0.001-4.88, Cr: 1.3-9.8, Mn: 0.1-0.6, Zn: 41-202, Ag: 0.002-1.5, Ba: 9.3-55.7, Fe: 8.5-236 mg/kg) does not vary as a function of the sampling area, except in the case of Ba and Zn. These metals registered the highest concentrations in muscles and gonads of organisms collected in areas of restricted circulation adjacent to oil platforms. Muscle and head of shrimp from three different areas were studied, and in general the highest values occurred in the head (Cu: 17.1-125, Pb: 1.7-13.1, Cd: 1.7-15.9, Cr: 1.2-15.9, Mn: 0.1-1.1, Zn: 55-161, Ag: 0.16-2.7, Ba: 11.6-90.6, Fe: 59-285), and no definite concentration trend was observed as a function of the area.

CONTINENTAL SHELF WATER

Data on metal concentration in the waters of the Gulf of Mexico is scarce. The inherent analytical difficulties to measure metals in seawater, as well as their concentration at mg L^{-1}as well as ng L^{-1} levels make analyses difficult.

Vázquez *et al.* (1991) analyzed the concentrations of Ni and V in water (surface and near-bottom) and in superficial sediments of the coast of Veracruz. The average concentration of Ni in water was 0.032 µg L^{-1}, ranging from 0.008 to 0.095 µg L^{-1}. The same authors recorded higher values on a cruise in December, which are attributed to the presence of northerlies, with clearly different results for surface and bottom water. The concentration of V in water ranged from 0.001 and 0.119 µg L^{-1}, with an average of 0.026 µg L^{-1}. In the November samples the values on the surface and the bottom were similar, whereas differences were observed in December and attributed to the northerlies that blew during the sampling activities. The Ni and V concentrations measured by Vázquez *et al*. (1991) in the Gulf of Mexico are lower than those reported by Auger *et al*. (1999) in the English Channel, of 0.02 mg L^{-1} for Ni and 1.10 mg L^{-1} for V.

Villanueva (2000), analyzed dissolved metals (Cu, Cr, Ni, V and Ti) in near-bottom water from four zones of the southern Gulf of Mexico: zone A, located near the discharge of the Grijalva-Usumacinta rivers; zone B, located inside the Petróleos Mexicanos (PEMEX; National Mexican Petroleum Company) exclusion zone, towards the southeast; zone C, located inside the PEMEX exclusion zone, towards the northeast; and zone D, located outside the PEMEX exclusion zone, in the carbonate province. The highest measured Cu values (Table 22.6) are in zone D, which also registered the highest levels of dissolved organic matter, with which Cu is associated. The highest values of Cr, Ni and Ti are found in zone A and are associated with discharges from the Grijalva-Usumacinta rivers. The highest value for V (28.7 µg L^{-1} on average) is found in zone C and is attributed to activities associated with the extraction of hydrocarbons.

CONTINENTAL SHELF SEDIMENTS

There are few studies of metal concentration in the continental shelf sediments of the Gulf of Mexico. Table 22.7 presents data from different sources on metal concentration in surface sediments of the Gulf of Mexico.

Vázquez *et al*. (1991) found concentrations of Ni between 82 and 113 mg/kg, with an average concentration of 95.5 mg/kg, on the coast of the state of Veracruz. The values are very similar for samples taken in November and December; samples taken the farthest away from the coast have the highest values, which is attributed to diagenesis processes. The concentrations of V in sediments from the area ranged from 39 to 63 mg/kg, with an average of 45.5 mg/kg. The values were very similar for the samples collected in both cruises.

Rosales *et al*. (1994) undertook studies in the Campeche Sound in order to evaluate the impact of oil exploitation activities in the area. They measured 18 mg/kg of Pb, and between 66 and 366

Table 22.6. Concentration of metals (μg L^{-1}) in water of the continental shelf of the Gulf of Mexico compared with other areas in the Western Hemisphere.

Area	Cu	Cr	Ni	V	Ti
Coast of Veracruz[a]	-	-	0.032	0.026	-
Campeche Bay A[b]	8.2	7.4	4.2	20.4	13.4
Campeche Bay B[b]	5.6	5.2	3.5	24.0	5.3
Campeche Bay C[b]	7.9	5.8	3.4	28.7	4.5
Campeche Bay D[b]	11.4	6.0	2.9	24.7	13.0
San Francisco Bay[c]	0.2-5.3	-	-	-	-
Trinidad, West Indies[c]	-	0.003-0.011	-	-	-
English Channel[d]	-	-	0.020	1.1	-

[a] Vázquez *et al.* 1991; [b] Villanueva-Estrada(2000); [c] Sadiq 1992; [d] Auger *at al.* 1999.

mg/kg of Cr with an average of 166 mg/kg. The distribution pattern of these metals suggests that the sources are the Grijalva-Usumacinta rivers. This is supported by the relationship with the Al discharges, which is an element of terrigenous origin. The Ba found in the area exhibits distribution patterns that could be related to oil exploration and exploitation activities, with the highest values (767 mg/kg) measured adjacent to oil exploration areas.

Ponce (1995) undertook a study of surface sediments along the continental shelf of Tamaulipas. The highest metal concentrations are associated with the mouth of the Soto la Marina River, with the exception of Cr which exhibits its highest value in the extreme north of the study area. The same author collected samples of surface sediment on the continental shelf of the state of Veracruz, opposite the mouth of the Coatzacoalcos and Tonala rivers, and of Laguna del Carmen. The highest values occurred to the south of the mouth of the Río Coatzacoalcos, near the coast (Table 22.7). Surface sediments opposite the mouth of the Río Grijalva were also studied, where the highest values occurred at stations located further away from the coast. Of the three areas of the continental shelf included in the study (Tamaulipas, Veracruz and Tabasco), the highest levels of Ni, Zn and Cr were found in the continental shelf off the state of Tabasco, Cu and Pb in the south of Veracruz, and Cd on the continental shelf off Tamaulipas.

Twenty six sediment cores of 10 cm were collected from the continental shelf off Campeche during February 1992 (Macias *et al*. 1999), and the concentrations of Cu, Ni, Zn, Cr, Cd, Pb, V, Mn and Fe were measured. The majority of the metals exhibited higher concentrations towards the southwest of Campeche Bank, and low concentrations towards the Yucatán shelf. Table 22.7 shows the average concentration for each metal and its corresponding range. The distribution pattern of the metals suggests that their concentration is controlled in great part by the proximity to sources of terrigenous material. Apparently, the distribution gradients are affected by the circulation patterns.

Table 22.7. Metals in sediments (mg/kg) of the Gulf of Mexico.

Area	n		Cu	Cd	Cr	Zn	Pb	Ni	V	Ba	Fe
Veracruz Coast[a]	31	Average	-	-	-	-	-	95.5	45.5	-	-
		Range	-	-	-	-	-	82.0-113.0	39.0-63.0	-	-
Southeast Gulf of Mexico[b]	37	Average	-	-	166	-	18	-	-	147	-
		Range	-	-	83-316	-	-	-	-	33-767	-
Continental shelf - Tamaulipas[c]	23	Average	15.23	9.14	36.97	71.67	4.22	26.82	-	-	-
		Range	3.20-24.98	2.80-18.00	nd-74.96	17.30-115.7	nd-6.90	1.90-76.00	-	-	-
Continental shelf - Veracruz[c]	29	Average	17.94	1.79	15.6	33.18	15.2	17.86	-	-	-
		Range	1.6-91.25	1.16-5.96	nd-50.3	nd-185.9	nd-37.7	3.40-84.80	-	-	-
Continental shelf - Tabasco[c]	32	Average	16.88	7.03	101.7	84.4	6.44	91.0	-	-	-
		Range	nd-33.50	2.80-13.90	57.8-157.4	47.3-127.9	nd-27.20	45.7-147.4	-	-	-
Continental shelf - Campeche[d]	26	Average	7.53	0.09	39.8	18.5	4.3	-	47.78	-	1.84
		Range	3.80-18.70	0.01-0.70	3.0-100.0	0.04-79.6	0.22-20.2	-	15.60-117.5	-	0.0-7.9
Southeast Gulf of Mexico - Rivers[e]	18	Average	-	-	-	79.7	-	-	-	751.0	3.79
		Range	-	-	-	45.4-116.7	-	-	-	256.4-2909	2.60-5.30
Southeast Gulf of Mexico - Lagoons[e]	14	Average	-	-	-	10.4	-	-	-	472.0	-
		Range	-	-	-	0-85.2	-	-	-	106.8-864.0	-
Southeast Gulf of Mexico[f]	28	Average	9.4	3.45	74.5	64.6	107.0	71.3	33.9	35.5	7.0
		Range	0.05-18.3	0.05-6.82	54.7-97.3	0.54-131.0	67.3-263.0	1.54-211.0	17.7-59.6	9.3-74.6	1.8-13.0
USA[g]		Average	35	0.48	110	140	43	34	-	-	-

[a] Vázquez *et al.* (1991); [b] Rosalez *et al.* (1994); [c] Ponce (1995); [d] Macias *et al.* (1999); [e] Rosalez *et al.* (1999); [f] Vázquez *et al.* (2002); [g] O'Connor and Cantillo (1992).

The Fe and Zn values show high variability, whereas Cu, Cr and Cd show little variation. The normalization of the studied metals with respect to Fe shows that this element is controlling the distribution of most metals. A linear regression analysis of this relationship suggests the presence of three areas, especially in the cases of Cr, Ni and Zn: one of high metal concentration, one of low metal concentration and a transition area.

The analysis of the distribution of metals throughout 10 cm of core 5A (located approximately at 19° 24' latitude and 92° 38' longitude), did not exhibit notable changes, which suggests the absence of diagenesis processes, with the exception of Cd. In the case of core 5B (located approximately at 20° 05' latitude and 91° 52' longitude), perturbations were observed at 4-5 cm depth for all studied metals, suggesting a common event such as a fluctuation in the riverine input or in the circulation regimen. The pattern of spatial distribution of metals suggests the influence of terrigenous material deposited in the coastal areas of Tabasco and Veracruz.

The distribution pattern for Ni/V exhibited the highest values in the restricted area for exploitation of hydrocarbons. This pattern could be associated with hydrocarbon extraction activities or with the circulation patterns in the area.

Rosales *et al*. (1999) collected 73 surface sediment samples in the southeastern Gulf of Mexico. The analysis of the textural characteristics of the surface sediments showed that muddy sediments originating from the Grijalva-Usumacinta river system were distributed towards the north and were later dispersed towards the northeast. This distribution pattern is associated with the dynamics of the area. Another less intense current, which flows towards the mouth of the Grijalva-Usumacinta rivers, is observed opposite Laguna de Términos Lagoon. These currents determine the distribution patterns of metals in the area.

The samples were classified for their Si/Al content in two groups with different chemical characteristics:

1) Sediments associated to the discharges of the Grijalva-Usumacinta rivers. These correspond to more weathered sediments with the highest content of Al, lower concentrations of Na and K, and a significant correlation of Al with Fe, Ti and Zn, suggesting that Fe is associated with the crystalline structure of the clay. Table 22.7 shows the metals content of these sediments.
2) Sediments with lower Al concentrations, which are associated with the discharges of Laguna de Términos. These sediments have a high correlation of Al with Si, and of Fe with Mn, Ti and Mg, which suggests the presence of heavy minerals that are highly resistant to weathering.

A factor analysis facilitates the observation of the presence of three types of sediment with different chemical characteristics: 1) terrigenous sediment associated with the discharges of the Grijalva-Usumacinta rivers, which are characterized mainly by their content of Al, Zn, Fe and K; 2) sediments with a high content of Ba, associated with hydrocarbons extraction activities; and 3) sediments associated with discharges from Laguna de Términos, which are characterized by their organic matter content.

In February/March 1997 Vázquez *et al.* (2002) collected 28 sediment samples in the southeastern Gulf of Mexico, from the mouth of the Río Coatzacoalcos to Laguna de Términos, concluding the following: the studied elements (Si, Al, Fe, Na, Mg, Ca, K), with the exception of Ca and Si did not exhibit a significant seasonal variation. The high concentration of CaO in the eastern region of the study area is caused by the nature of Campeche Bank, which is a carbonate province. The concentration of Si was higher in the western portion of the study area. The distribution of metals was random and did not follow a definite pattern. However, some metals such as Ni, V and Ba exhibited abnormally high values in some locations, suggesting that they could be associated with hydrocarbons extraction activities. No correlation was observed between the concentrations of metals and the composition of the sediments, which suggests that the metals are not associated to aluminosilicate minerals, iron hydroxides or carbonates that occur naturally in the area. The correlation between the metals indicates that Cu, Zn, Ni, Co and V in sediments are controlled by the same factors as the association to the surface of Fe oxides.

Comparing the values for metals measured in other areas, it can be observed that the concentrations of Cu, Zn and Cr are similar to the values obtained in coastal zones, but the concentrations of Cd, Pb and Ni are higher.

ARTIFICIAL RADIONUCLIDES

Rodríguez *et al*. (2002) studied the ^{137}Cs and ^{40}K isotopes in sediment cores from the southeastern Gulf of Mexico and found that the concentrations of these isotopes varied according to the sedimentary environment, but were similar to values reported in other parts of the world. The concentration of ^{137}Cs ranged from 2 to 6.5 Bk/kg and the concentration of ^{40}K ranged from 100 to 800 Bq/kg. The highest values of ^{137}Cs were found in the sediments from the delta of the Grijalva-Usumacinta rivers, at depths of 75 m; these values are associated to the large amount of rainfall in the area (3,000 mm/year) and the size of the basin of the Grijalva-Usumacinta rivers, which is much bigger than the Río Panuco basin. The highest values of ^{40}K occurred in the delta of the Río Panuco, with sediments that come from the Sierra Madre Oriental and the central part of Mexico, where there is intense agricultural activity and use of fertilizers. The lowest values of ^{137}Cs and ^{40}K occurred in the Yucatán slope.

The study of radioisotopes enables the continental shelf of the Gulf of Mexico to be differentiated by depositional environments from each region, for which reason it is not possible to generalize about the biogeochemical processes of metals from one oceanic region to another.

CONCLUSIONS

The absence of effective programs for monitoring and control of metals in the Mexican coastal environment, the increasing industrialization and urbanization of the Mexican coastal zone and, most importantly, the lack of a thorough application of environmental regulation, have led to the presence of Pb, Cd and Cr in 45% of the rivers and lagoons of the Gulf of Mexico. The most affected areas are Laguna del Ostión, Laguna Alvarado, and Río Coatzacoalcos in Veracruz, and the Laguna de las Ilusiones, Laguna El Yucateco and Laguna Julivá in Tabasco.

The data analyzed in this study demonstrates a trend for the increase of metals levels, mainly Pb and Cr, which have values up to 20 orders of magnitude higher than concentrations reported in the last two decades.

The high level of metals in the coastal areas of the Gulf of Mexico are mainly due to the continuous and massive input of wastewaters from coastal cities, industrial effluents from mining, tanning and galvanizing activities, as well as fertilizer plants, varying with the periodicity and magnitude of discharges. Finally, the atmospheric emissions that originate in the urban and industrial regions of coastal cities are another important source of contamination. Therefore, the information presented here shows that the trend of metal contamination in the coastal zones of the Gulf of Mexico is increasing, mainly for Pb, Cd and Cr, which can produce toxic effects to the organisms that inhabit the Mexican coastal zone and, therefore, have an adverse effect on the important fisheries of the region, such as those from Laguna La Mancha, Laguna Mandinga and Laguna del Ostión Lagoons in Veracruz, and the Carmen-Pajonal-Machona lagoon system in Tabasco.

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