Monitoring ecosystem health of the Terminos Lagoon region using heavy metals as environmental indicators

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Abstract

The Terminos Lagoon region is one of the most important biodiversity hotspots of Mexico and Mesoamerica. However, this high biodiversity is threatened by the activities of the Mexican oil industry, urban development, and land use change in the watersheds of the rivers that drain into it. This study presents the results of a monitoring program undertaken from 2006 to the present using heavy metals (Cd, Pb, Hg, Cu, Zn, As, Al, V and Cr) as environmental indicators. Heavy metals were measured in water, sediments and oysters as sentinel organisms, three times a year for 15 different sites. Eventually, metals concentration has been measured on selected marine-estuarine organisms (shrimp, fishes, sea turtles, dolphins, and manatees) to see the effect of bioaccumulation. Although heavy metals levels remained in low concentrations in water, some samples of oysters and mammals presented contamination levels above Mexican Legislation, suggesting effects of bioaccumulation.
Keywords: heavy metals, pollution, Terminos Lagoon.

1 Introduction

Heavy metal contamination in coastal environments has increased globally in the last decades (Fowler [1], Caeiro *et al.* [2], Vicente-Martorell *et al.* [3]). This trend is especially true for coastal lagoons and estuaries, which biochemical processes serve as an efficient trap for contaminants, especially heavy metals

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(Birch [4]). Because these high concentrations of contaminants can have toxic effects on aquatic and human organisms (Mountouris *et al.* [5]), heavy metal contamination is one of the biggest threats to the costal environment.

The Terminos lagoon and associated wetlands are one of the most important ecological and fishing regions of Mexico. The primary productivity of this ecosystem extends to the adjacent marine ecosystem, and close to 80% of the fish in the Campeche Sound depend on the lagoon for reproduction and food (Sánchez-Velasco *et al.* [6]). In terms of biodiversity, the Terminos lagoon is one of the most extensive wetlands (5,000 km^2), best conserved and most important in Mexico and in Mesoamerica. Five hundred and sixty nine species of plants, 207 species of molluscs, 15 species of crustaceans, 125 species of fish, 45 species of amphibians, 134 species of reptiles, 328 species of birds and 134 species of mammals were recorded (INE [7], CONANP [8]). Because of this high biodiversity, the region was declared as a National Protected Area of Flora and Fauna in 1995 and is recognized as a priority area by the Tripartite Committee of Mexico-Canada-US for bird conservation in North America, by the RAMSAR Convention, and by the Counsel for North American Wetland Conservation.

The socio-economic development in the Terminos Lagoon has increased considerably in the last few decades due to the growth of the oil industry (Vazquez-Luna [9]). Worldwide, Mexico ranks third place in oil production, first place in offshore oil production, and ninth in crude reserves. Currently, 80% of its production comes from the Terminos Lagoon region and adjacent marine area. One of the consequences of this increase has been the heavy metal contamination, which anthropogenic input has exceeded natural levels derived from geological processes (Vázquez *et al.* [10], Sastre Conde *et al.* [11], Gold-Bouchot *et al.* [12]). However, studies to date have only been determined in isolated sites and substrates, making it difficult to determine trends, causes and consequences. As such, the present study presents results of the distribution of heavy metals in different water levels, sediments and organisms, measured continuously over the last 6 years.

2 Methods

2.1 Monitoring program background

The Terminos Lagoon Monitoring Program (TLMP) implemented in 2006 has focused on measuring contamination levels in three strata: the water column, sediments and sentinel organisms.

The water column substrate was chosen for the TLMP because it is where primary productivity occurs for the marine-estuarine ecosystem, and it is the origin of many marine-estuarine food webs (Sánchez-Velasco *et al.* [6]). Because heavy metals in the water column often bind to sediments and suspended organic matter, and are subject to movements of water bodies, measuring the water column can present a snapshot of the concentration of heavy metals and its influence of its distribution by coastal dynamics.

The second substrate analyzed in the TLMP is the marine-estuarine sediments, which are a crucial ecological component of nutrient recycling and also initiate food webs, as for shrimp (Ramos-Miranda *et al.* [13]). Being comprised of inorganic components, particulate matter and organic material, sediments are able to bond with heavy metals to form more complex matter. As such, sediments form the natural reservoir for these contaminants and provide useful information on the long-term effects of contamination (Ridgway and Shimmield [14]).

The final substrate monitored was the sentinel organisms. The oyster, *Crassostrea virginica*, was selected because it is able to bioconcentrate contaminants, has low metabolic rates and abundant populations in the lagoon (Goldberg and Bertine [15]). Occasionally, heavy metal concentrations have been determined in white shrimp (*Litopenaeus setiferus*), fish (*Dorosoma petenense*), sea turtle eggs (*Eretmochelys imbrincata* and *Chelonia mydas*), dolphins (*Tursiops truncatus*) and manatees (*Trichechus manatus manatus*), in order to assess bioaccumulation of heavy metal contamination at the top of the food chain.

In order to have a more holistic view of pollution levels, we determined non-essential metals such as Cd, Pb and Hg, as being toxic in an aquatic environment, as well as metals essential for biological systems, such as Cu, Zn and As, which can become toxic at high concentrations. Similarly, in order to get an overview of the geochemical processes in the lagoon, we determined the concentrations of Al as indicator of river runoff (Rosales-Hoz *et al.* [16]), while V and Cr were used as indicators of oil activities.

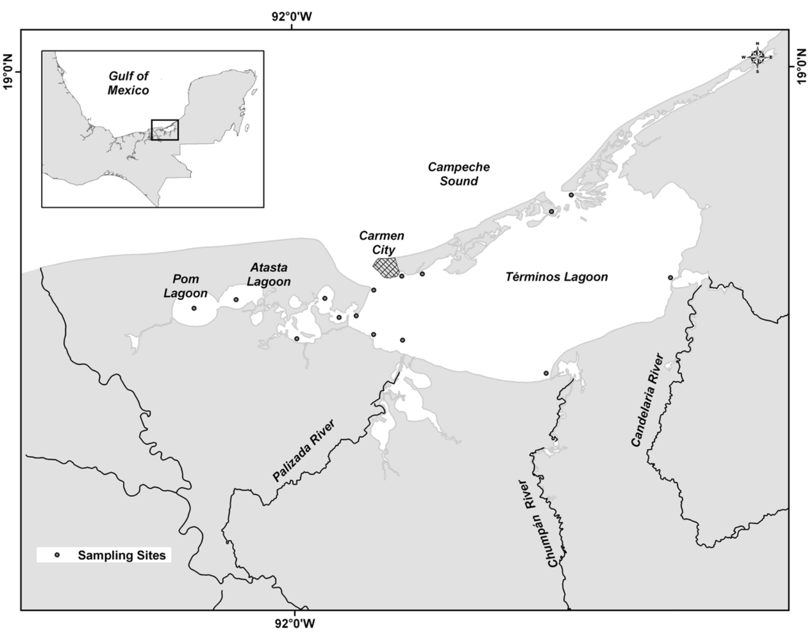

Figure 1: Sampling locations in the Terminos Lagoon.

To obtain a representative sample of each substrate, 15 sites were selected in the Terminos lagoon (Fig. 1). Samples of the water column, sediments and oysters were collected in the three distinct regional seasons (dry, wet and *nortes*).

2.2 Determination of metals

Water column samples were collected with a Van-Dorn bottle, placed in polyethylene flasks and preserved at 4ºC for further analysis. Once in the laboratory, organic material was removed from the samples by UV irradiation using a Metrohm Digester model 705.

Sediments were collected using a geological dredge, ensuring the sample was never in contact with the metal part of the equipment. Sediments were placed in plastic bags and preserved at 4ºC for further analysis. Once in the laboratory, samples were dissolved in by adding a mixture of concentrated HNO_3, HF and HCl and placed in a microwave (MARS 5 Xpress) according to EPA 3051 method. At the same time, separated sediments samples were dried at 60ºC to determine organic matter content following Walkey-Black method (Gaudette *et al.* [17]).

At each sampling site (Fig 1), 10 random oysters were collected and placed in plastic bags at 4ºC. In the laboratory, tissue homogenates of the oyster bodies were performed and dissolved in a microwave (MARS 5 Xpress) according to EPA 3052 method.

In addition to determining heavy metals in oysters, sea turtle eggs were collected in 2009 on beaches in the region for contaminant analysis. En each site, 10 un-hatched eggs were collected during the nesting season, corresponding to the months of April through October. Similarly, in 2011, white shrimp and fishes were collected during the rainy season by dragging nets. That same year during the *nortes* season, blubber and skin samples were collected from live dolphins and manatees using a 67 kg crossbow and modified arrows (Ibarra-Vargas *et al.* [18]). The shrimp, dolphin and manatee samples were kept frozen until analysis. These samples were later processed according to EPA 3051 method.

Heavy metals in water, sediment and organisms were determined by Voltammetry (797 VA Computrace), using a rotating gold electrode for Hg determinations, and the Hanging Mercury Drop Electrode method for all other metals.

2.3 Statistical analysis

Data were analyzed in Statistca® using a Pearson's linear correlation to determine the relationship between heavy metal concentration and amount of organic material. Correlation coefficients were considered significant at $p < 0.05$.

For each season (rainy, dry and *nortes*), a cluster analysis was used to group areas with similar characteristics. The resulting maps were analysis using the Spatial Analysis tools in ArcGIS 9.3 to determine spatial and temporal components.

3 Results and discussion

3.1 Non-essential metals: Cd, Pb and Hg

Two thirds of the water column samples did not have detectable levels of Cd. The concentration of this metal varied between <0.0002-0.005 ppm, with a mean of 0.0001 ppm (Table 1). Similarly, the majority of the sediment samples did not have detectable levels of Cd, however, the samples that did contain this metal had levels 50 to 700 times higher than those found in the water column (max 0.28 ppm, mean of 0.0836 ppm).

Table 1: Heavy metals in the Terminos Lagoon (ppm); ND = Not detected.

		Non-Essential			Essential		Environmental Indicators	
Substrate		Cd	Pb	Hg	Cu	Zn	Al	Cr
Water	Mean	0.0001	0.0023	0.0001	0.0106	0.1034	ND	0.0101
	Max.	0.0050	0.0090	0.0085	0.0780	0.5190	ND	0.0300
	Min.	ND	ND	ND	ND	0.0236	ND	0.0005
Sediment	Mean	0.0836	0.7034	0.0287	1.2764	6.6745	26.897	0.8203
	Max.	0.2800	1.9102	0.2489	3.5790	26.396	37.560	6.0666
	Min.	ND	ND	ND	0.0028	0.1026	19.560	0.5280
Oyster	Mean	0.0130	0.1762	0.0001	0.3844	5.6989	22.054	0.5471
	Max.	0.1152	1.2881	0.0004	0.5640	24.612	29.200	1.1430
	Min.	ND	ND	ND	0.0023	1.0553	16.530	0.0263
Shrimp	Mean	0.1027	ND	ND	7.1339	7.8942	15.666	0.7586
	Max.	0.3854	ND	ND	42.802	25.419	24.847	3.5528
	Min.	ND	ND	ND	ND	0.8333	10.106	0.3655
Dolphin	Mean	0.3269	0.1111	ND	12.991	9.1140	4.4357	0.6969
	Max.	2.0710	1.0020	ND	82.025	24.442	12.135	1.0390
	Min.	ND	ND	ND	ND	1.5640	0.6530	0.2030
Turtle	Mean	ND	ND	0.3735	1.3076	27.932	ND	6.4649
	Max.	ND	ND	0.4897	2.0892	29.699	ND	7.9765
	Min.	ND	ND	0.2234	0.6607	25.353	ND	4.0394
Manatee	Mean	0.0159	0.2646	ND	0.3822	6.0948	17.479	0.7830
	Max.	0.0317	0.5292	ND	0.6876	10.230	26.887	0.8409
	Min.	ND	ND	ND	0.0768	1.9587	8.0714	0.7251
Fish	Mean	ND	ND	ND	35.179	8.2621	11.038	10.797
	Max.	ND	ND	ND	58.306	10.944	15.197	16.904
	Min.	ND	ND	ND	12.051	5.5799	6.8804	4.6904

With respect to Cd in sentinel organisms, only one third of the samples did not have detectable levels. Oysters with Cd had levels 25 times higher than those found in the water column (max 0.1152 ppm, mean of 0.013 ppm). For the other organisms, no Cd was detected in fish or sea turtle eggs; however, shrimp, dolphin and manatees had mean concentrations of 0.1027 ppm, 0.3269 ppm and 0.0159 ppm of this metal respectively.

Most samples taken from the water column had detectable levels of Pb, ranging from <0.0002-0.009 ppm, with an average of 0.0023 ppm. Similar to Cd, Pb levels in sediments were at least 200 times higher than in water (from <0.0002-1.9102 ppm; mean of 0.7034 ppm), while concentrations of in oysters increased 75-150 times from values reported in water (<0.0002-1.2881 ppm, mean of 0.1762 ppm). No detectable levels of Pb were found in shrimp, sea turtle eggs or fish. Only body tissue samples from dolphin and manatee had Pb concentration ranging from <0.0002-1.002 ppm, with a mean of 0.1111 ppm, and <0.0002-0.5290 ppm, with a mean of 0.0159 ppm, respectively.

Most of the water column, sediments and oysters samples had non-detectable levels of Hg. Maximum values for these substrates were 0.0085, 0.2489 and 0.0004, respectively. This metal was also undetectable in shrimp, dolphin, manatee and fish samples. Only turtle eggs had Hg concentrations ranging from 0.2234-0.4897 ppm, with a mean of 0.3735 ppm.

Mexican legislation does not have limits for Cd, Pb or Hg concentrations in sediments. Only laws NOM-001-ECOL-1993 and NOM-027-SSA1-1993 indicate that the maximum allowable limit for these metals in the water column is 0.0002 ppm for Cd, 0.01 ppm for Pb and 0.0001 for Hg, while levels in organisms should not exceed 0.5 ppm for Cd, 1.0 ppm for Pb and 1.0 for Hg. Most values detected in this paper were below these limits. However, two samples of water, and four samples of oyster, both took in 2006, had levels above legislation limits. Also, samples from dolphin took in 2011 were above these standards.

3.2 Essential metals: Cu, Zn, and As

The minimum, maximum and average values of essential metals in the water column are shown in Table 1. These values increased 60 to 120 times in sediments and between 10–50 times in oysters. Levels of Zn found in shrimp, sea turtle eggs, manatee and dolphin were similar to the values generally found in sentinel organisms. Cu concentration exceeded by far values found in oysters, increasing 500-1000 times the values found in water.

Mexican legislation does not establish permissible limits for the essential metals measured in this paper for sediments or sentinel organisms, and the permissible levels in the water column are established for human consumption. However, the levels found of these metals in sediments and in oysters were lower or similar to values reported in previous studies (Rosales-Hoz *et al.* [16], Vázquez *et al.* [10], Sastre Conde *et al.* [11], Gold-Bouchot *et al.* [12]).

3.3 Environmental indicators

Vanadium was only detected in samples of dolphin, fish and manatee sampled in 2011, showing no specific environmental pattern. Al was strongly associated with the discharge from the Palizada and Candelaria rivers (Fig. 2), which are the major sources of fresh water for the lagoon. This association was more evident in the sediments than in the water column or sentinel organisms, and was directly correlated with the concentration of organic matter ($p < 0.05$).

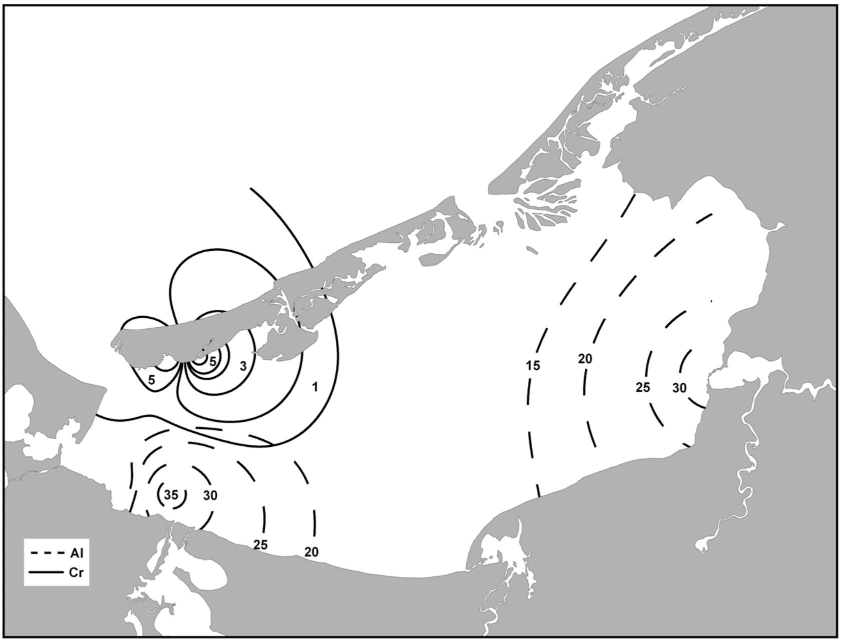

Figure 2: Concentration (ppm) of Al and Cr in sediments of the Terminos Lagoon.

3.4 Spatial and temporal distribution of pollutants

Spatial analysis of concentration maps showed that in general, the highest values of Cd, Pb and Cr in sediments and in sentinel organisms were found near the urban area of Carmen City, suggesting an anthropogenic source (Fig. 2 and 3). Carmen City is the major urban area in the region (population of 195,000) and focuses the majority of its port activities and services in the oil industry. Other areas of high heavy metal concentrations were the Pom lagoon and the town of Atasta, where oil activities such as oil *Cantarell* nitrogen plants and pipeline from the Campeche Sound are found.

Figure 3: Concentration (ppm) of Pb, and Cd in sediments of the Terminos Lagoon.

Although the majority of fresh water discharge occurred at the end of the rainy season, the heavy metal concentration in the water column did not always coincide with this season, possibly because of dilution or because the highly dynamic system did not permit the establishment of clear patterns.

The largest concentration of heavy metals in organisms occurred during the dry season, possibly because of the high metabolic rates that the organisms exhibit during that season as a response to high temperatures and salinity.

Considering that some metals such as Pb and Cd are from anthropogenic sources, and that their point of entry into the system is via the water column, it appears that there is a potential for accumulation of these metals in the organic matter of sediments, where the concentration of these metals was on average 100 times higher than in the water column.

Similarly, if we consider that the organic matter of sediments is the major source of food for shrimp (Ramos-Miranda *et al.* [13]), and this crustacean is in turn the major source of food for dolphins (Delgado-Estrella [19]), it becomes apparent that bioaccumulation could occur with some metals at the top of the food chain. Following the food chain for water-sediment-shrimp-dolphin, the concentration levels of Cd and Pb increased 100-2500 times at the top of the food chain. Although the values in the water are on average 10 times below the maximum permissible level for Mexican legislation, the levels in dolphins are above the levels for the same established regulations.

4 Conclusions

For the last six years most water samples had heavy metal concentrations under the maximum levels established by Mexican legislation.

Concentration of metals in sediments increased in average 250 times those concentrations found in water.

Higher levels of Cd and Pb found in dolphins and manatees suggest an effect of bioaccumulation through the food chain.

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