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Total Metals in Intertidal Surface Sediment of Oyster Culture Areas in Sonora, Mexico

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Metals are introduced to the aquatic ecosystem as a result of human activities, as well as from soil and rock weathering. Since they are persistent and because of the potential environmental effects, humans and marine ecosystems are susceptible to these effects by metals through the trophic chain (Gonzalez et al. 1998).
Metals are found in all phases of aquatic ecosystems (Gonzalez et al. 1998), dissolved in water, accumulated by biota, and usually at higher levels in the sediment (Menzer 1991). The concentration of metals in these three phases can vary as result of physicochemical conditions (Burton 1991) and climatic variations, such as "El Niño" (DeLong et al. 1991).

The state of Sonora is located in the Northwest of Mexico, with a surface area of 184, 934 km^2 and a coastline of 1200 km. Sonora has a great diversity of industrial activities like mining, agriculture, livestock, and important tourist resorts. Sonoran coastal waters are also characterized by an exceptionally high capture of commercial fish and shellfish and are among the most prolific producers of cultivated oysters in Mexico (García-Rico et al. 2001).

During 1998-1999, a high mortality rate of cultivated oyster was observed in the estuarine systems of the coast of Sonora within the Gulf of California (Sea of Cortez). This phenomenon was observed right after the worst recorded climatic changes caused by "El Niño" of 1997-1998. However, there are no information on other factors, such as the concentration of metals in the estuarine system of this region, that might have contributed to the high mortality of oyster. The aim of this work was to provide information on the concentration of metals in marine sediment in order to have additional information that contribute to the understanding of such high mortality rates.

MATERIALS AND METHODS

Surface sediments were collected from four locations along the Sonoran coast (Fig. 1) from February to August 1999. Sampling sites were located in four different districts (Puerto Peñasco site 1, Caborca site 2, Hermosillo site 3, Guaymas site 4). The sites were selected according to their proximity to potential

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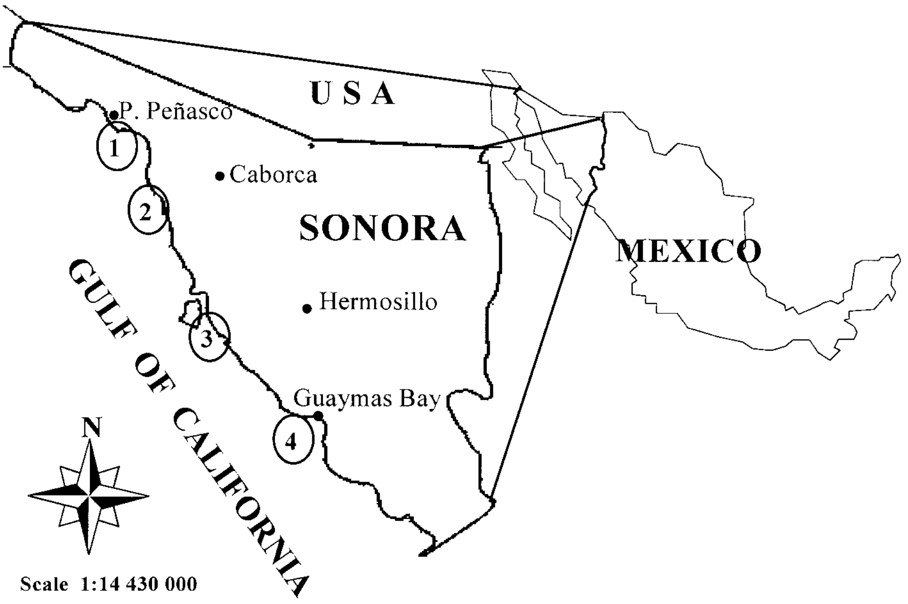

Figure 1. Localization of study areas in Sonoran coast

pollution sources and to oyster culture areas. During each month, sampling was repeated one to three times at low tide. A total of seventy-one samples were collected. Water temperature ranged between 15.8 and 30.3°C and salinity was 35.7-40%. The particle size (>63 μm sieve) of surface sediments was mostly sand (>85%). Surface sediments were collected using plastic spoons, transferred to polyethylene containers, and transported on ice to the laboratory. Samples were dried in an electric oven for 24 h at 55°C, ground through a 1 mm sieve and stored at –20°C until analysis.

Total metal concentrations in ground sediments were determined by atomic absorption spectrometry (SpectrAA-20, Varian) after microwave digestion (MDS-81D, CEM) according to García-Rico et al. (2001). Organic matter was determined by wet oxidation method (Méndez et al. 1998) and carbonates were estimated according to Kot et al. (1999). For quality control, Standard Reference Materials from NIST (e.g., estuarine sediment 1646a and domestic sludge 2781), as well as blank and duplicate measurements were carried-out during the complete procedure. Percent recovery means for NIST SRM were: Cd (94.1), Cu (90.4), Zn (89.5), Pb (103), Hg (109) and As (101). Detection limits (μg/g dry wt) were determined by the blanks method (USP XXII, 1990): Cd (0.0024), Cu (0.0014), Zn (0.0072), Pb (0.0017), As (0.0056), and Hg (0.0048). To avoid metal contamination, plastic and glassware were cleaned with HNO_3 and rinsed with double distillated water. Statistical analyses were conducted using ANOVA, Tukey-Kramer and Fisher's LDS mean comparisons, and Pearson correlations (NCSS 1996).

RESULTS AND DICUSSION

Metal concentrations found in Sonoran sediment samples are shown in Table 1. Zn was the most abundant element in sediment (27.5 μg/g), followed by Pb, Cu, As, Cd, and Hg. These concentrations were similar to those reported for uncontaminated or low metal polluted areas (Rosales et al. 1994; Méndez et al. 1998). Zn showed wide variation, ranging from 6.49 to 390 μg/g. This behavior could have been a consequence of both the large sampling area and different degrees of pollution in the localities examined. The highest value for Zn corresponded to a sample located to the North of the state.

Of the nonessential metals (Table 1), Pb showed the highest mean values (14.4 μg/g). The highest Pb concentration (33.5 μg/g, $p \leq 0.05$) was detected to the South (Fig. 2) of the state (site 4), which is located close to an important tourist area. Similar behavior was observed for Cd and Cu. These metal concentrations were lower than those reported previously by Hosch (1996) in sediments from Guaymas Bay. Site 4 is a small bay within the Guaymas Bay surrounded by mountainous natural barrier.

Guaymas Bay is one of the most important harbors in Northwest México, with important industrial development, tourist activities and high human population density, all these factors possibly impact the area. The highest organic matter level (1.39%) was found in site 4. Organic matter levels for all other areas ranged from 0.97 to 1.09%. Due sediments of the present study were mostly sand, metal concentrations might be relate with organic matter levels. Metal distribution and bioavailability in sediments are driven by organic matter concentration and more recently it has been suggested that metal bioavailability may be controlled by acid volatile sulfide (Burton 1991; Ramos et al. 1999a). Metals are also, associated with labile components like carbonates and aluminosilicates which are coated with iron/manganese oxides (Burton 1991; Ramos et al. 1999a; Davis 2000). Another factor accounting for these metal concentrations is the natural composition of the seashore rock formations. Soil composition of the area is volcanoclasic lower tertiary with high carbonate levels in site 4 (44.6 %); carbonate levels for the rest of study areas ranged from 3.93 to 7.78%. Carbonates are known to affect considerably the sorption behavior of cationic species, like trace elements in aquatic environments, limiting their metal mobility (Davis 2000).

Table 1. Metal concentrations (μg/g dry wt) in sediments collected along the Sonoran coast.

Metal	Mean	Median	Range
Cadmium	1.04	1.00	0.50 - 2.51
Copper	5.06	4.00	1.50 - 27
Zinc	27.5	18	6.49 - 390
Lead	14.4	12.3	2.50 - 33.5
Mercury	0.07	0.05	0.01 - 0.35
Arsenic	3.25	3.08	0.09 - 7.71

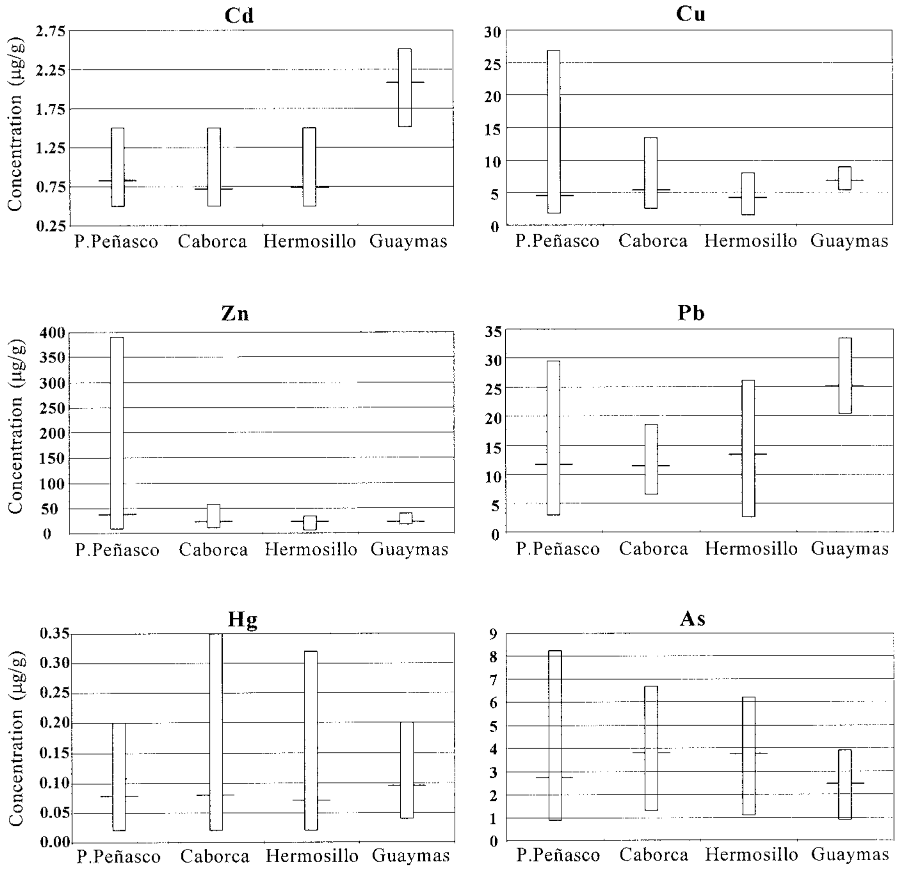

Figure 2. Concentration of metals (µg/g dry wt), in sediments by sampling stations (□ range; — mean).

Other authors have reported high Cd and Zn concentrations in sediments along the Gulf of California (Méndez et al. 1998). They propose that the accumulation of metals in the trophic chain can be explained by atmospheric routes and/or by marine current transport. The extensive discharge from the Colorado River into the Gulf of California during 1950-1960 (Da Costa Gomez and Valle 1989) could have contributed to the increase in metal concentrations. The Gulf of California has marine streams that produce large water movements, especially in the north of the Gulf. During natural events like "El Niño" high water temperatures are observed which could result in depletion of nutrients and the consequent reduction of plankton (DeLong et al. 1991), these changes might affect the concentrations of available metals to the food chain.

Two sites of high As contamination ($p \leq 0.05$) were site 2 and site 3 as shown in Fig. 2. Both sites are located close to natural mineral deposits and to an important agricultural zone. Some areas of Sonora such as Caborca, are naturally rich in As, measurements of this cation in well water were found to have two times the recommended As levels (Wyatt et al. 1998).

The highest levels ($p>0.05$) of Hg were detected in sites 3 and 4. Hg is associated with environmental pollution, its use in agriculture is widespread. One of the problems is the incorporation of metallic Hg by microorganisms to form methyl mercury produces a very toxic compound. In this study, the mean Hg concentration ($p>0.05$) was 0.07 μg/g with the highest level in site 3 (0.35 μg/g). Hg concentration found in this district was higher than that reported by Kot et al. (1999) in marine sediments (0.05 μg/g) from La Paz Lagoon, Baja California, México. However, the levels found in the present study corresponded to natural levels for uncontaminated marine deposits (0.06 to 0.55 μg/g). These concentrations of Hg are also lower than average abundance of this element in sedimentary rocks (0.4 μg/g) and soils (0.01 to 0.8 μg/g) (Kot et al. 1999).

Ramos et al. (1999a) have suggested that a consistent association between particular groups of metals such as Cu:Zn, Cd:Zn, and Cu:Cd may indicate particular biochemical pathways or reflect their common source. Significant correlations ($p\leq0.01$) between Cu:Zn ($r=0.81$), Cd:Pb ($r=0.83$), Pb:Cu ($r=0.54$), Cu:Cd ($r=0.33$), As:Cu ($r=0.35$), and As:Zn ($r=0.40$) were found. The high correlation for these metal can be explained by the fact that Sonora has a great diversity of mineral deposits that could provide a natural source of metal in this coastal areas.

Metal concentrations found in monthly sediment samples are shown in Fig. 3. The lowest mean levels for all metals were detected in February and increased in March. The highest levels of Cu, Zn, and As were observed during July and August (these are also the rainy season). These metal concentrations in the rainy season may be attributed to freshwater runoff from the land. Between April and August all metals showed a non-significant variation, except Cd, Zn and Pb. Páez-Osuna et al. (1990) reported higher metal concentrations during summer when higher temperature and salinity occur.

Since the sediments are substrate for oyster culture, it is noteworthy to mention that oyster mortality was first observed in March, 1997 and by June it reached 90 %. At the initial stages, high mortality was observed mainly in the oyster larva, but by the summer, mortality occurred at all grown stages. Our results show the presence of background levels of metals in sediments from oyster areas.

Metal toxicity is modificated by temperature changes, metal stable complexes like metal-carbonate, metal-organic matter, and metal-oxides (David 2000). When metal mean concentrations of this study were compared to Effects Range Low (ERL) and Lowest Effect Level (LEL) sediment toxicity values reported by Ramos et al. (1999b), all concentrations found (except Cd for LEL) were lower than both ERL and LEL. Monitoring the sediment and water column concentrations of Cd and other cations, is import for filtering organisms, such as oysters, since available metal concentrations are also affected by pH and salinity. Metal levels in sediment from the Sonoran coast were mostly similar to those reported in the Gulf of California and were in agreement (except for Cd) with the earth's crust (Rosales-Hoz et al. 1994), therefore metals don't appear to be involved in oyster mortalities.

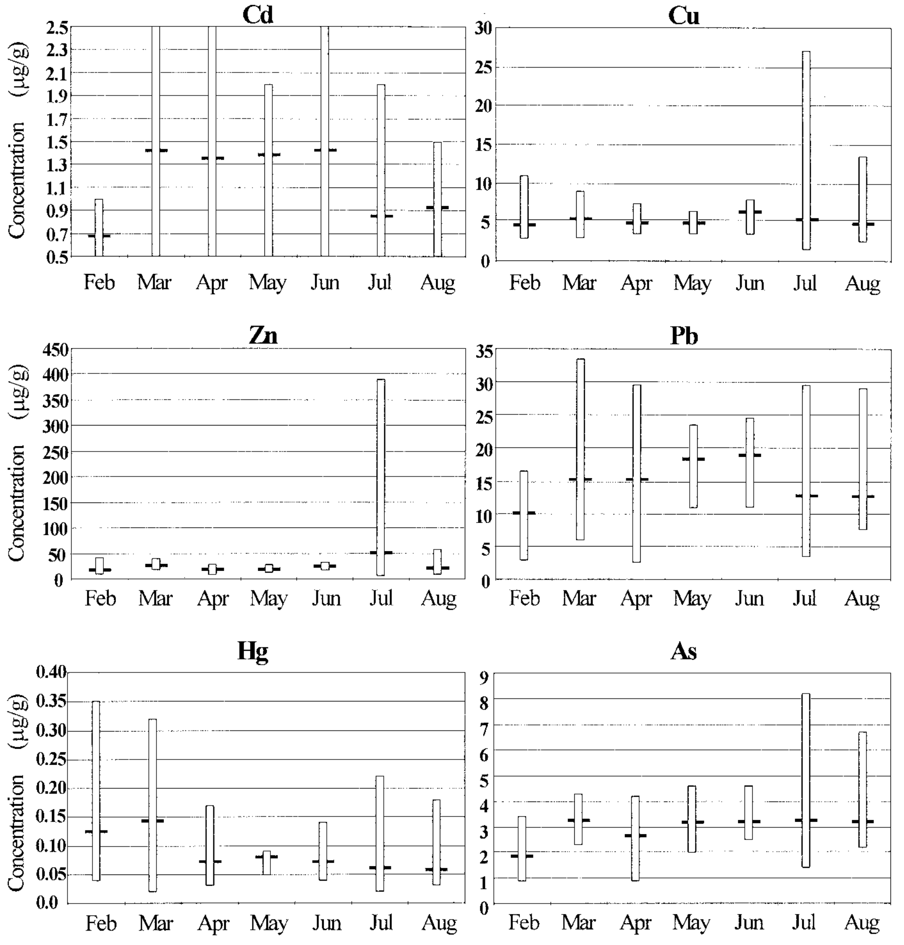

Figure 3. Concentration of metals (µg/g dry wt), in sediments by sampling months (▯ range; — mean).

More studies are required to identify Cd sources and its bioavailability. Further work in this area may prove useful in providing information about the environmental and man-made factors involved in heavy metal toxicity in marine species. This toxicity may also affect marine resources in terms of biological conservation and the quality of the seafood produced.

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