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Heavy Metal Distribution in Surface Sediments from a Subtropical Coastal Lagoon System Associated with an Agricultural Basin

C. Green-Ruiz, F. Páez-Osuna

Institute of Marine Sciences and Limnology, National Autonomous University of Mexico, Mazatlán Academic Unit, Post Office Box 811, Mazatlán, 82000, Sinaloa, Mexico

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Agricultural fertilizers are considered as important sources of heavy metals input in soils (Alloway, 1990), which are eroded and carry out to catchment basins where they are adsorbed by particulate material mainly organic matter and sediments. Therefore, heavy metal assessment in sediments plays a key role for the identification of pollutant sources in aquatic systems. Altata-Ensenada del Pabellón (AEP) lagoon system on the northwest coast of Mexico, (Fig. 1) have a surface of 335 km^2. The main water body is connected with three inner shallow lagoons (< 1 m deep); Bataoto (2 km^2), Caimanero (3 km^2) and Chiricahueto (18 km^2), which directly receive agricultural and sugar cane industrial discharges. The AEP lagoon system also receives the effluents from 130000 ha of agricultural fields where different crops (vegetables, sugar cane, corn and soybeans) are cultivated and from municipal untreated sewage from Culiacán City and towns around it (800 000 inhabitants). Previous investigation (Green-Ruiz and Páez-Osuna, 2001) reported heavy metal anomalies in the study zone, considering several normalization criteria. The present work addresses the heavy metal distribution in surface sediments from this coastal complex lagoon establishing their relationship with anthropogenic sources.

MATERIALS AND METHODS

Bottom water and surface sediment samples were obtained from 77 sites in the AEP coastal lagoon system (Fig. 1), with an horizontal Niskin bottle and a Van Veen grab (0.1 m^2), respectively. Water sample aliquots were taken during sunlight hours (8:00 – 17: 00 h), in order to determine immediately dissolved oxygen concentration (Riley and Chester, 1989) and, at the laboratory, salinity with an induction salinometer Beckman model RS9. A small amount of sediment was carefully removed and a sample (0-5 cm) was taken from the middle of the grab using a plastic spatula in order to prevent metallic contamination. After, the samples were placed in acid washed plastic bags (HCl 2M, HNO_3 2M) and refrigerated until returned to the laboratory.

Representative portions of the sediment samples were oven-dried at 60 ºC. A pre-weighed dried sample was wet-sieved to determine the amount of sand (2000-63 μm) and mud (<63 μm) size material. In addition, silt (63-4 μm) and clay (<4 μm) percentage were determined using pipette method (Folk, 1974). About 10 g of se-

Correspondence to: C. Green-Ruiz

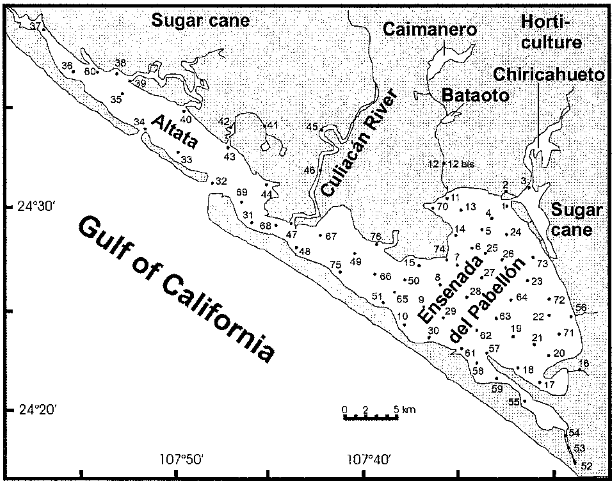

Figure 1. Localization of sampling sites into Altata-Ensenada del Pabellón coastal system.

diment were finely ground for geochemical analysis. Organic carbon content was analyzed by the chromic acid oxidation method (Loring and Rantala 1992). Calcium concentration was quantified by atomic absorption spectrometry after digestion of calcium with sodium acetate, adjusting to pH 5 with acetic acid and it was considered as associate with carbonate, thus calcium carbonate was calculated (Green-Ruiz, 1996). Al, Co, Cu, Cr, Fe, Li, Mn, Ni, Pb, V and Zn concentrations were also determined by atomic absorption spectrometry, but after digestion with inverted aqua regia (HNO_3: HCl 3:1) (Breder 1982). The performance of this methodology was verified, analyzing the marine sediment reference material SDN-1/2 (IAEA, 1985) and the accuracy of the metal concentrations was satisfactory, except for Pb (141 % of recovery). Analytical precision of replicates (n=6) varied from 2.3 to 15.4 % relative to standard deviation. In order to find the correlation existing between variables, linear regressions were made and an r coefficient matrix created. The study area was divided in three subregions: (1) Altata Bay (AB), (2) Ensenada del Pabellón (EP), and (3) inner lagoons (IL). Differences in average concentrations among these subregions were assessed by an one-way analysis of variance and the Tukey's multiple comparison test (Zar, 1984), using the GraphPad Prism 2.0 for Windows 97 (GraphPad software Inc., San Diego, CA).

RESULTS AND DISCUSSION

Average values of dissolved oxygen concentration and salinity in water, and organic carbon, calcium carbonate and heavy metal contents and textural composition of sediments from the three subareas: AB, EP and IL (the last including Culiacan river and the little estuaries) are shown in Table 1. Except for heavy metals, spatial distribution maps and discussion of these parameters are shown in Green-Ruiz (1996). There were not significant differences between the mean dissolved oxygen concentrations into the lagoon system. Levels lower than

0.03 mg/l were evidenced in stations 11 and 12. On the other hand, there was a significant difference between the mean value of salinity from AB (34.25 ± 0.97) with EP (23.43 ± 4.97 ‰), whereas that the lowest salinities were found in IL.

Table 1. Mean (± SD) concentrations of OD, salinity, Mzϕ, TOC, $CaCO_3$, and heavy metals in the sediments of the three regions from Altata Bay-Ensenada del Pabellón lagoon system. Means differ signicant ($p < 0.05$) among regions.

	AB	EP	IL	Whole
OD (mg/L)	6.1 ± 1.0	6.0 ± 1.2	5.7 ± 3.1	6.0 ± 1.6
Salinity	34.3 ± 1.0[a]	23.4 ± 5.0[a]	21.0 ± 12.5	25.9 ± 7.5
Mzϕ (Ø)	2.3 ± 1.6[ab]	4.7 ± 2.1[a]	4.8 ± 2.4[b]	4.2 ± 2.3
TOC	0.8 ±0.90[b]	1.6 ±1.6	2.4 ± 1.1[b]	1.5 ± 1.5
$CaCO_3$	2.8 ± 2.9[a]	7.5 ± 11.2[a]	2.8 ± 3.7	5.9 ± 9.5
Al (%)	2.7 ± 1.6[ab]	5.0 ± 2.0[a]	5.0 ± 2.2[b]	4.6 ± 2.1
Co (ppm)	15.4 ± 5.9	18.1 ± 5.6	17.5 ± 3.4	17.4 ± 5.5
Cr (ppm)	13.4 ± 3.0[ab]	16.2 ± 4.1[a]	16.8 ± 3.1[b]	15.7 ± 3.9
Cu (ppm)	15.2 ± 12.0[ab]	32.1 ± 14.4[a]	36.8 ± 13.1[b]	29.3 ± 15.5
Fe (%)	4.5 ± 1.9	5.9 ± 2.3	4.7 ± 1.7	5.4 ± 2.2
Li (ppm)	11.9 ± 6.6[a]	20.9 ± 9.4[a]	21.5 ± 9.9	19.1 ± 9.6
Mn (ppm)	436 ± 229[a]	884 ± 768[a]	1826 ± 2324	925 ± 1127
Ni (ppm)	9.3 ± 7.5[a]	16.2 ± 7.9[a]	15.7 ± 6.2	14.7 ± 8.0
Pb (ppm)	81.3 ± 32.6[a]	140.1 ± 58.0[ac]	91.6 ± 32.1[c]	121.0 ± 56.7
V (ppm)	28.9 ± 8.3	35.9 ± 11.2	36.7 ± 6.6	34.6 ± 10.4
Zn (ppm)	57.2 ± 41.8	84.5 ± 36.7	96.1 ± 41.4	80.5 ± 40.0

Significant differences among: [a]AB and EP; [b]AB and IL; [c]Ep and IL.

Sediments in AB consisted primarily of sand, with a mean grain size of 2.3 ± 1.6 Ø, being significant lower than the mean for EP (4.7 ± 2.1 Ø) and IL (4.8 ± 2.4 Ø), where the highest standard deviation occurred, suggesting a low-energy environment because the semi-enclosed nature. Organic carbon contents into the whole AEP coastal system ranged from 0.2 to 11.5 % with a mean of 1.5 ± 1.5 %. The greatest organic carbon concentration took place around IL, while the middle ones in EP. In AB region, where marine conditions prevail, only close to the mouths of little estuaries showed high values. The calcium carbonate content varied between 0.5 and 46.7 %, with an average of 5.9 ± 9.5 %. There was a significant difference between the mean of this parameter at EP and AB, being higher at the former, because the settlement of organism with calcareous shells in this region. Table 2 shows correlation coefficients between salinity, dissolved oxygen, organic carbon and calcium carbonate contents, grain size mean and metal concentrations. Mapping of the distribution of heavy metals in the sediments are presented in Figs. 2 and 3.

Al ranged from 1.2 to 9.9 % averaging 4.6 ± 2.1 % (Fig. 2a). It is a major constituent of fine-grained aluminosilicates with which the bulk of the trace metals

Table 2. Correlation coefficients between dissolved oxygen concentration, salinity, organic carbon content, mean grain size and heavy metals concentrations ($P \leq 0.05$; $^{*}P \leq 0.001$).

	Al	Co	Cr	Cu	Fe	Li	Mn	Ni	Pb	V	Zn
OD	-----	-----	-0.25	-----	-----	-----	-----	-----	-----	-----	-----
Salinity	-0.41*	-----	-0.32	-0.49*	-----	-0.33	-0.55*	-0.30	-----	-----	-----
Mzϕ	0.83*	0.51*	0.69*	0.93*	0.55*	0.95*	0.29	0.86*	0.58*	0.55*	0.79*
TOC	0.45*	0.50*	0.62*	0.65*	0.24	0.54*	-----	0.54*	0.30	0.45*	0.55*
$CaCO_3$	-----	-----	-----	-----	-0.29	-0.25	----	-----	-----	-----	-0.23
Al	1.00	0.55*	0.66*	0.83*	0.57*	0.81*	0.37*	0.71*	0.47*	0.45*	0.69*
Co		1.00	0.58*	0.58*	0.35	0.53*	-----	0.45*	0.35	0.46*	0.44*
Cr			1.00	0.76*	0.51*	0.70*	0.24	0.65*	0.58*	0.55*	0.64*
Cu				1.00	0.55*	0.91*	-----	0.85*	0.57*	0.60*	0.81*
Fe					1.00	0.63*	-----	0.58*	0.43*	0.56*	0.52*
Li						1.00	-----	0.88*	0.59*	0.60*	0.82*
Ni								1.00	0.60*	0.58*	0.75*
Pb									1.00	0.47*	0.53*
V										1.00	0.61*

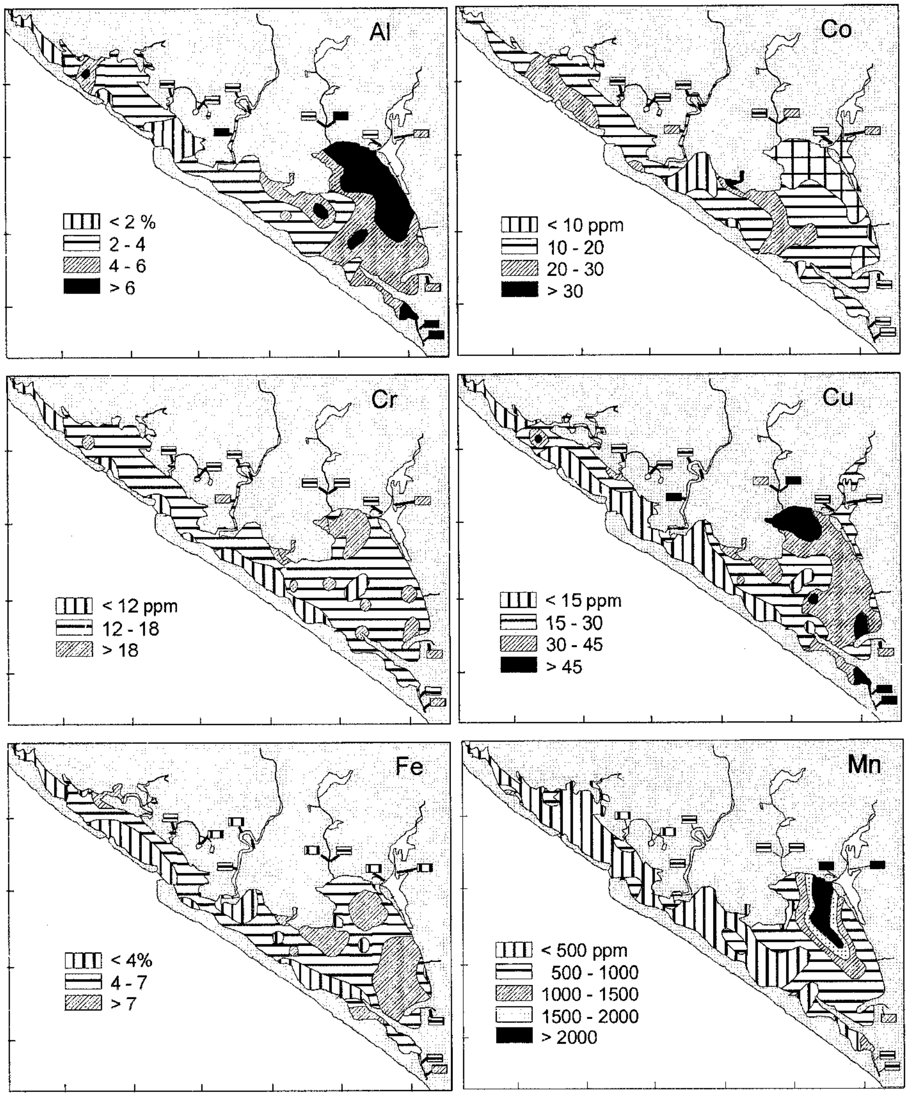

Figure 2. Spatial distribution of Al, Co, Cr, Cu, Fe and Mn concentration in sediments from Altata-Ensenada del Pabellón coastal system.

are associated (Loring, 1991). In the studied area, there was a strong correlation between this metal and the other trace element analyzed. In addition, Al is highly refractory and its concentration is generally not influenced by anthropogenic sources (Schropp and Windom, 1988). Co concentrations varied between 8.2 and 37.1 ppm with an average of 17.4 ± 5.5 ppm, which is higher than that found in phosphated fertilizer (1-12 ppm) (Alloway, 1990). The highest Co concentrations were present in the east portion of EP as well as at north of the AB region (Fig. 2b). Cr contents varied from 8.9 to 28.0 ppm averaging 15.7 ± 3.9 ppm. Northern and southern portion of EP showed the highest values (Fig. 2c). However they were lower that the concentration of this metal found in phosphated fertilizer (66 and 245 ppm; Alloway, 1990). The lowest Cu concentration was 5.6 ppm and the highest one was 63.8 ppm with an average of 29.3 ± 15.5 ppm. The highest values were found on both the northern and southern margins of EP (Figure 2d). In addition to natural source, metallic fungicides with high content of Cu (cupravit) are used on the agricultural fields around the lagoon system. Moreover, Alloway (1990) mentioned that for phosphated fertilizer levels of 300 ppm of Cu could be presented.

Iron concentrations ranged from 2.0 to 13.5 % with an average of 5.4 ± 2.2 %. It have an homogeneous pattern, however the highest content of this metal were presented near to the east margin of EP (Fig. 2e). Mn concentration varied between 97 and 8166 ppm with an average of 925 ± 1127. Mn pattern was different of the other metals studied, It showed correlation with Al ($r=0.37$, $P \leq 0.001$) and $Mz_{\emptyset}$ ($r=0.29$, $P \leq 0.05$); however, there were not association with organic carbon. Fig. 2f shows a distribution that suggests clearly an input of manganese from Chiricahueto lagoon in the north portion of Ensenada del Pabellón because to the agricultural effluents derived mainly from the vegetable fields, which are characterized by the use of large quantities of fertilizers and pesticides, particularly metallic fungicides with high content of Mn (maneb, manzate). The average concentration of Ni was 14.7 ± 8.0 ppm, with the highest value of 30.5 ppm (Fig. 3a). High correlation of Ni with Cu (r 0.85) and Al ($r=0.71$) suggest the same principal source. However, greatest values of this metal could be associated with boat traffic and agricultural effluents.

Concentrations of Pb varied between 46 and 294 ppm, with an average of 121 ± 57 ppm. The highest values were found at the east portion of EP (Fig. 3b), where the hunting club exists and probably leaded bullets are influencing the found levels. Another possible source of Pb is the atmospheric transport from vehicle emission from Culiacán city and several roads surrounding the study area. The minimum value of V concentration was 10.0 ppm while the maximum one was 66.4 ppm, averaging 34.6 ± 10.4 ppm. Highest concentrations were present in the southeast portion of EP as well as at the center of the AB region (Fig. 3c), associated with channel entrances from agricultural fields. Alloway (1990) reported V contents ranging from 2 to 1600 ppm in phosphated fertilizer. Zn concentration varied from 18.8 to 176.1 ppm with an average of 80.5 ± 40.0 ppm. (Fig. 3d). The distribution pattern of this metal shows a clearly release from the agricultural fields, where the use of fungicides with high concentrations of Zn (zineb), has been reported. Additionally, phosphated fertilizer have Zn concentration varying between 50 and 1450 ppm (Alloway, 1990) and could be contributing to the Zn load in the study area.

In oxic environments, Mn-oxides can be formed and they are the natural oxidants of the low soluble Cr(III) species, which is adsorbed in the sediment, to the high soluble Cr(VI) which is transferred to the adjacent water (Guha et al., 2000). This can indirectly explain the inverse correlation between Cr and dissolved oxygen. Al, Cr, Cu, Mn and Ni showed inverse correlation with salinity, possibly as a result from the deprotonation of the iron hydroxide surfaces of the clays by sodium chloride present

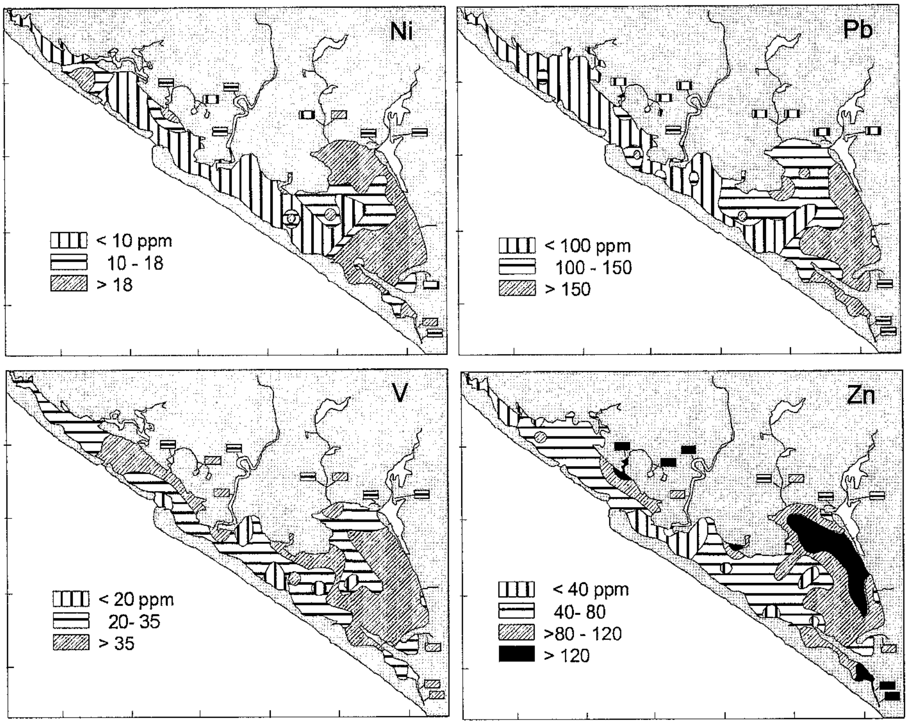

Figure 3. Spatial distribution of Ni, Pb, V, and Zn concentration in sediments from Altata-Ensenada del Pabellón coastal system.

in saline water, which creates electrostatic repulsion between the trace elements and the clay mineral surfaces (Luoma et al., 1995), inhibiting metal sorption on this important sediment site.

According to Summers et al. (1996) and Zhang et al. (2002), the surface area of the sediment particles depends of grain size and controls the metal adsorption processes. Consequently, this explains the correlation found between all the metals studied and grain size. Organic matter is also recognized as a preferential site for metal because its ability of complexation and adsorption, which leads to a strong correlation between it and metal elements (Gonzales et al., 1991; Ergin et al., 1996). This direct correlation was evidenced for all the metals, except Mn that possibly is forming oxides and does not attach to the organic compounds. Fe and Zn presented inverse correlation with calcium carbonate because the dilution effect of this parameter (Ergin et al., 1996), suggesting a possible terrestrial source for these three metals.

With the exception of Cu, Fe, V and Zn, all the metals showed higher mean concentration in EP than in AB. In addition, Al, Cr, and Cu average contents also were higher in IL than in AB. Finally, the mean concentration of Pb in EP was higher than that in IL. In general, highest metal concentrations were associated with agricultural discharges by little estuary runoffs and the Culiacán River mouth.

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