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Heavy metal anomalies in lagoon sediments related to intensive agriculture in Altata-Ensenada del Pabellón coastal system (SE Gulf of California)

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Abstract

Heavy metal concentrations were examined in surface sediments from 79 sites within the Altata-Ensenada del Pabellón lagoon system. Data were normalized to separate natural from anthropogenic factors using aluminum and lithium as conservative elements and following two different discriminating criteria. For the normalization process, the natural metal concentrations were assumed to vary consistently with aluminum and lithium, unless the metal contents were of human origin. Strong linear correlations ($P < .001$) were observed between the conservative elements and the metals measured. According to Szefer's normalizing criteria, about 90% of the polluted sites, for at least one metal, occurred near agricultural discharge drains. In accordance with the Müller [Umschau 79 (1979) 778.] scale, this lagoon system is subject to pollutant effects only with regard to Pb (moderately to strongly polluted). It was concluded that either Al and Li could be useful to normalize granulometric variability in heavy metal studies of these lagoon sediments, and that Summers' normalization criterion proved more rigorous than Szefer's for these types of sediments. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Heavy metal; Normalization; Enrichment factor; Coastal lagoon; Gulf of California

1. Introduction

A characteristic feature along most Mexican coasts is the presence of numerous coastal lagoons, e.g., from the Colorado River in Sonora to San Blas in the state of Nayarit, there are about 35 lagoon systems. These ecosystems embrace a great variety of habitats that include mangrove forest, salt marshes, intertidal pools, swamps, freshwater inner lagoons, brackish and sea water systems; all possessing a high biological diversity and a rich and complex food chain (Flores-Verdugo et al., 1996). These ecosystems constitute important fishery and nursery grounds, and some of which include human settlements (Páez-Osuna et al., 1998a). In fact, the more important ports and coastal towns in Mexico have grown up around or near lagoon systems, which are consequently ecosystems influenced by anthropogenic activities.

The Altata-Ensenada del Pabellón lagoon–Culiacán River system is located in the central portion of the Sinaloa State littoral, on the northwest coast of Mexico, from 107°30′ to 107°58′W and from 24°20′ to 24°40′N (Fig. 1), having a surface area of 335 km^2. This water body is connected with several channels (termed "esteros") and inner shallow lagoons (< 1 m deep), which receive agricultural and sugar cane industrial discharges. The major source of pollution is represented by waste effluents from intensive agricultural activity (273,000 ha) around the lagoon system, consisting mostly of vegetables and sugar cane (Páez-Osuna et al., 1998b). In fact, it is known (Unión Nacional de Organismos Productores de Hortalizas y Frutas (UNPH), 1988; International Atomic Energy Agency (IAEA), 1990) that large amounts of pesticides and fertilizers are used in this region, mainly, organophosphorous, carbamates, and metallic fungicides (e.g., Maneb, Zineb, Cupravit). On the other hand, Culiacán River carries sediment into this lagoon system. This sediment arises from tertiary to cretaceous age acid igneous rocks, which are both intrusive and extrusive, cropping up in the Sierra Madre Occidental, where there are Au, Ag, Cu, Pb, and Fe ores (Anonymous, 1978). In addition, sewage discharges from Culiacán City (750,000 inhabitants), and small towns (100,000 inhabitants in total), flow into this river. More-

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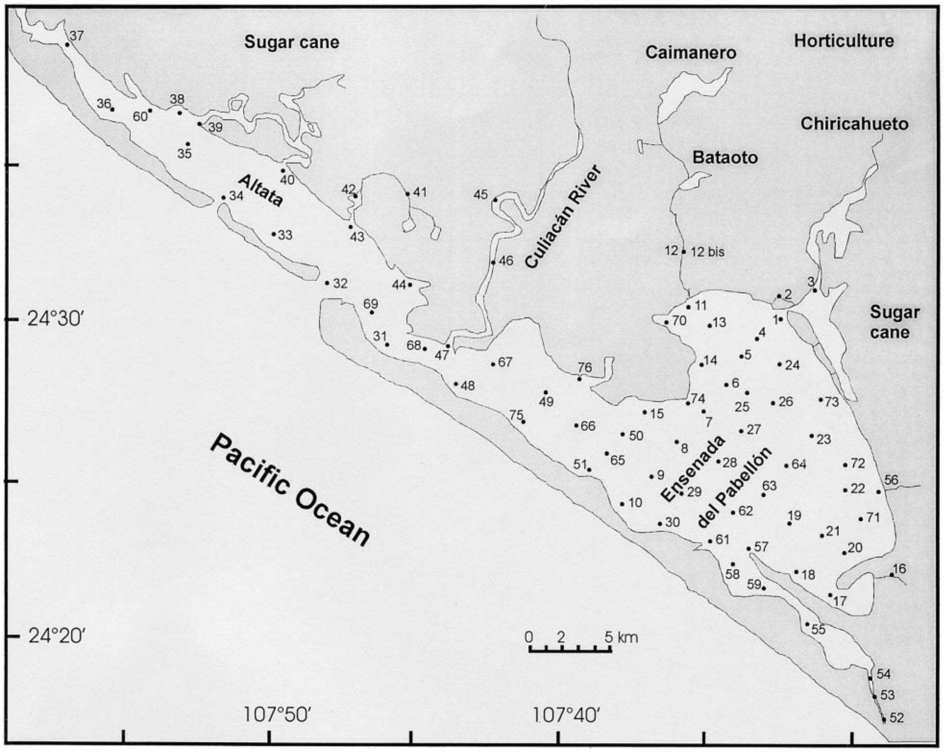

Fig. 1. Altata-Ensenada del Pabellón lagoon system, Mexico. Numbers indicate sampling stations.

over, commercial molluscs, fish, and shrimp are caught in the lagoon system for human consumption.

Early studies (Paéz-Osuna et al., 1992; Readman et al., 1992; Carvalho et al., 1996) showed that sediments and organisms collected from Altata-Ensenada del Pabellón are contaminated with phosphorus and pesticides. In other studies (Páez-Osuna et al., 1993a,b, 1994), metal concentrations in oysters, clams, and mussels were examined, revealing that organisms sampled in 1990 had higher Cd, Cu, Fe, and Zn contents than those from 1998 to 1991. The former year was characterized by rain, and the sites, with relatively high heavy metal levels, were associated with discharges from agricultural fields and regional runoffs. The comparison of metal levels among clams from different locations of Altata-Ensenada del Pabellón showed moderate contamination with most of the metals analyzed (Cu, Fe, Mn, Ni, and Zn).

Metal loads from natural and anthropogenic sources accumulate together, therefore, in order to differentiate the proportion of the element concentration coming from natural sedimentary sources from the anthropogenic proportion, normalizing tools are needed. To reduce the heavy metal variability caused by grain size and mineralogy of the sediments, and to identify anomalous metal contributions, geochemical normalization has been used with various degrees of success by employing conservative elements, such as Al (Schoer et al., 1982; Din, 1992; Szefer et al., 1995, 1996; Summers et al., 1996), Li (Loring, 1990), Fe (Szefer, 1990a,b; Herut et al., 1993; Tam and Yao, 1998), Rb (Grant and Middleton, 1990), and Sc (Ackermann, 1980). The normalizing element must be an important constituent of one or more of the major trace metal carriers and reflect grain size variability in the sediments (Loring, 1990). The choice of the conservative element is not universal, but depends mainly on the study area and the human activities that are involved.

Aluminum, which is one of the most important constituents of the aluminosilicate mineral fraction, is often used as a conservative element (e.g., Schropp et al., 1990; Din, 1992; Cortesäo and Vale, 1995; Summers et al., 1996). However, Loring (1990) has shown that lithium is superior to aluminum for the normalization of metal data from sediments derived mainly from the glacial erosion of crystalline rocks and is equal or superior to aluminum for those derived from noncrystalline rocks. Covelli and Fontolan (1997) consider that, for estimating anthropogenic inputs, it is more useful to calculate the nondimensional enrichment factor (EF) (Buat-Mènard, 1979; Zhang, 1995). On the other hand, the degree of metal pollution is divided into seven different classes according to the index of geoaccumulation (Müller, 1979), which has been used by several authors (e.g., Carruesco and Lapaquellerie, 1985; Pons et al., 1988).

In this study, heavy metal concentrations in sediments from Altata-Ensenada del Pabellón were examined and normalized using Al and Li as conservative elements employing two different discriminating criteria: (1) regional anomalies (Szefer et al., 1995, 1996), and (2) 95% prediction intervals (Summers et al., 1996). Additionally, the EF and the geoaccumulation index (I_{geo}) were also estimated for the elements analyzed.

2. Methodology

2.1. Sampling

Surface sediment samples were obtained from 77 sites in the Altata-Ensenada del Pabellón lagoon–Culiacán River system and two upstream sites (Humaya and Tamazula) in September 1991 with a Van Veen (0.1 m^2) grab sampler (Fig. 1). The sediments, which were in contact with the grab walls, were carefully removed and the sample was taken from the middle of the sediment package using a plastic spatula in order to prevent metallic contamination. After this, the samples were placed in plastic bags previously washed in acid (Moody and Lindstrom, 1977) and kept frozen until analysis.

2.2. Granulometric and geochemical analysis

Representative portions of the samples were oven-dried until constant weight at 60°C. The amount of sand (2000–63 μm) and mud size (< 63 μm) material in each sediment sample was determined by wet-sieving, and silt and clay percentage were determined by using the pipette method (Folk, 1974).

Each sediment sample was finely ground for geochemical analysis. Aliquots of 0.5 g were analyzed for organic carbon content by a chromic acid oxidation method (El-Rayis, 1985; Loring and Rantala, 1992), and the heavy metal concentrations were determined by atomic absorption spectrometry, after digestion with inverted aqua regia (HNO_3/HCl 3:1) as described by Breder (1982). The accuracy of the methodology was verified by analyzing the marine sediment reference material SDN-1/2 (International Atomic Energy Agency (IAEA), 1985), and agreement among the values obtained for the concentrations of each heavy metal determined in our laboratory for SDN-1/2 sediment and their corresponding values were satisfactory, with the exception of those for lead, which were overestimated (recovery, 141%) (Table 1).

2.3. Data processing

In order to find the interrelationships among variables, correlation analysis between the two conservative elements (Al and Li) and every metal analyzed were made and an r coefficient matrix was created. Regression analyses were run for all the metals using Al and Li as the independent variables. According to the Szefer et al. (1995, 1996) criteria, a regression line with its twice standard deviation band was drawn to define the natural geochemical population. The basis for this is that there is a 95% probability that points falling within this interval belong to the normal population (Motulsky, 1995), and those outside to an anomalous population. Otherwise, the Summers et al. (1996) criteria were used. After regression analysis, points falling out of the 95% confidence limit were eliminated to ensure that any statistical relationships found among metals and the conservative element were based solely on natural concentrations. After this, all eliminated points that were omitted from the regression analysis are included in the regression plots and concentrations of the metal, which fall above the upper 95% confidence limit, are considered enriched.

Table 1
Heavy metal concentrations in SDN-1/2 reference material

Element	Certified values[a]		Found here
	Average	Range	average ± S.D.[b]
Co	12.1	11.2–12.7	12.0 ± 0.6
Cr	149	125–161	129 ± 16
Cu	72.2	68.1–75.2	74.6 ± 3.7
Fe	3.64	3.53–3.78	3.76 ± 0.8
Mn	777	728–801	746 ± 70
Ni	31	27–34	29.3 ± 1.3
Pb	120	112–132	169 ± 11
Zn	439	432–452	440 ± 46

[a] IAEA (1985).
[b] Standard deviation.

Normality was tested by the Kolmogorov–Smirnov test (Zar, 1984) using the GraphPad Prism 2.01 for Windows 95 (GraphPad Software, San Diego, CA). Natural log transformations for Mn concentrations and square root for Li contents were needed.

EF is an index of contamination for a sediment sample, with respect to regional values, which indicates that when EF = 3, the element concentration is three times higher than the calculated baseline for the study area (Covelli and Fontolan, 1997). In this study, the EF formula (Buat-Mènard, 1979) was calculated using the heavy metal average concentrations of upstream sediments from the Humaya (25°05′42N and 107°24′27W) and Tamazula rivers (24°48′39N and 107°09′05W) as baseline levels, according to Forstner and Wittmann (1979), who used data from rocky material near study sites as the baseline (Eq. (1)):

$$\mathrm{EF} = [\mathrm{M}]/[\mathrm{Al\ or\ Li}]\ (\text{studied area sediments}) \, /[\mathrm{M}]/[\mathrm{Al\ or\ Li}]\ (\text{baseline}) \quad (1)$$

Where [M] is the metal studied. Likewise, in order to determine the extent of pollution in the Altata-Ensenada del Pabellón lagoon, the index of geoaccumulation introduced by Müller (1979) was used (Eq. (2)):

$$I_{geo} = \log_2([\mathrm{M}]\ (\text{studied area sediments}) \, /1.5[\mathrm{M}]\ (\text{baseline})) \quad (2)$$

3. Results and discussion

Ensenada del Pabellon region presents different types of sediments: sands predominate in the portion close to the

Table 2
Correlation coefficients of organic carbon content, mean grain size, and heavy metal levels ($P < .001$)

Element	Al	$Li^{1/2}$
Co	0.55	0.54
Cr	0.66	0.71
Cu	0.83	0.92
Fe	0.57	0.65
ln(Mn)	0.58	0.46
Ni	0.71	0.88
Pb	0.47	0.59
Zn	0.69	0.83
Organic carbon	0.45	0.54
$M\phi$	0.83	0.95

mouth of the Culiacan River. In the center of the lagoon, sandy silts are the main deposits while in the east portion, nearest to the agricultural fields, clayey silts and silty clays are present. The average of organic carbon content in the study area is 1.18%, increasing with the percentage of fine-grain sediments (Páez-Osuna et al., 1998b). Inner lagoons and small channels are characterized by relatively elevated organic carbon and silty sand sediments; while the Altata region, where marine conditions prevail [salinity 33–36 (Peraza–Vizcarra, 1973)], consists predominantly of sands with low organic carbon content.

All the metals, organic carbon, and mean grain size ($M\phi$) showed a high correlation ($P < .001$) with both Al and $Li^{1/2}$ (Table 2). Correlation coefficients for relationships between metals and $Li^{1/2}$ were slightly higher than those for associations with Al, except for Mn (in logarithm) and Co; which suggests that Li is a better normalizer than Al. Figs. 2 and 3 show the lineal regression analysis between metals and

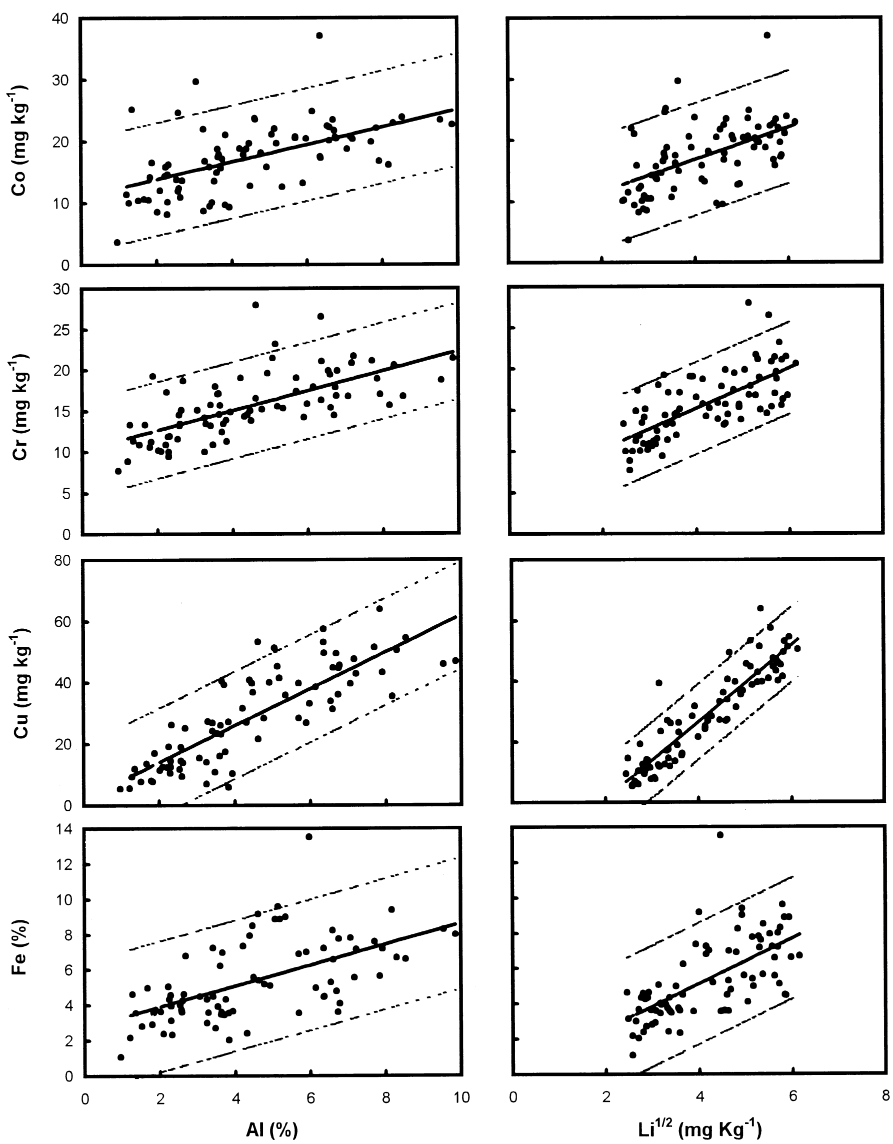

Fig. 2. Linear regressions for Co, Cr, Cu, and Fe concentrations as a function of Al (left) and $Li^{1/2}$ (right) concentrations. The regression line (solid) and twice standard deviation band (dashed lines) according to regional anomalies criterion (Szefer et al., 1996) are shown.

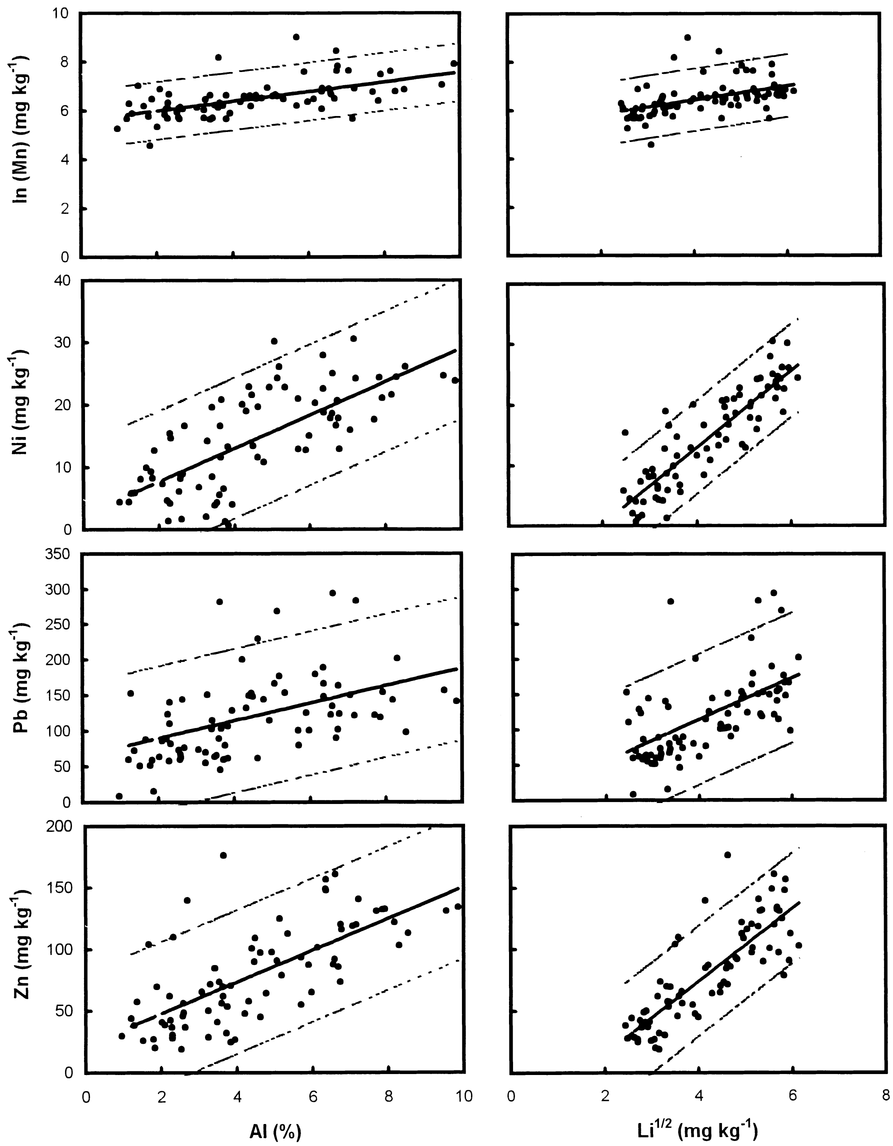

Fig. 3. Linear regressions for ln(Mn), Ni, Pb, and Zn concentrations as a function of Al (left) and $Li^{1/2}$ (right) concentrations. The regression line (solid) and twice standard deviation band (dashed lines) according to regional anomalies criterion (Szefer et al., 1996) are shown.

conservative elements (Al and Li) according to Szefer's criteria (regional anomalies). In general, except for Cu and Ni, both Al and Li vs. metals plots identify similar enriched stations. Data considered enriched for each metal by using this criteria represent between 1.3% and 6.3% of all the stations set with Al as conservative element, and 1.3–5.1% with Li (Table 3). A direct relation between stations considered to be enriched by metals and agricultural discharge drains was observed, except for Stations 29, 33, and 34, which were enriched with Co, and Stations 57 and 61 where anomalous values of Ni were detected. Stations 29, 57, and 61 are located in the southwest portion of the Ensenada del Pabellón, and Stations 33 and 34 near the lagoon mouth (Fig. 1).

Figs. 4 and 5 show the regression analysis of metals vs. Al and Li, using Summers' criterion (95% prediction intervals). This procedure was more rigorous than Szefer's strategy, since the data considered enriched for each metal by Summers' criteria represent between 8.9% and 45.6% of

Table 3
Percentage of stations considered enriched according to the conservative element and normalizing criteria

	Al		Li	
Element	Szefer's[a]	Summers'[b]	Szefer's	Summers'
Co	5	42	5	42
Cr	5	39	4	37
Cu	3	44	4	34
Fe	4	37	3	41
Mn	4	35	4	30
Ni	1	41	3	41
Pb	6	35	5	32
Zn	4	39	5	43

[a] Szefer et al. (1996).
[b] Summers et al. (1996).

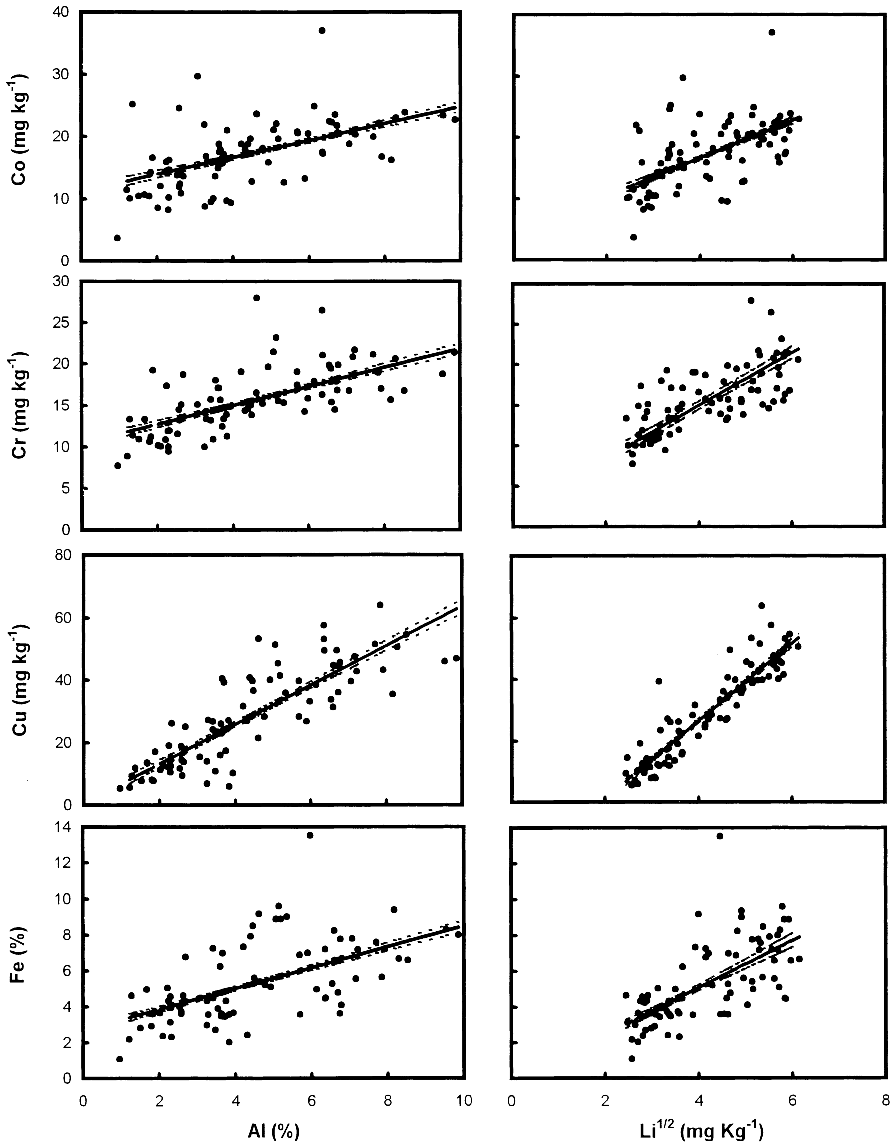

Fig. 4. Linear regressions for Co, Cr, Cu, and Fe concentrations as a function of Al (left) and $Li^{1/2}$ (right) concentrations. Plots show all points, including outliers that were omitted from the regression analysis. The regression line (solid) and 95% confidence band (dashed lines) according to Summers et al.'s (1996) criterion are shown.

the whole set of stations with Al as conservative element, and 10.1–43.0% with Li (Table 3). Moreover, 91% (Al as conservative) and 97% (Li as conservative) of all the stations were found enriched by at least one metal, while with Szefer's criteria, only 25% (Al) and 30% (Li) did.

Only Pb ($EF_{Al}=3.6$ and $EF_{Li}=5.4$) average concentrations showed enrichment in the Altata-Ensenada del Pabellón lagoon system (Table 4); although, Mn concentration for Stations 1, 2, and 3 presented EF values higher than 2. Stations with the highest EF values of Cr, Fe, Ni, Pb, and Zn were not identified as anomalous in regression analysis when Al was employed as conservative element. Similarly, Li follows the same trend for Co, Cr, Fe, and Pb. This clearly indicates that the strategies involved are not consistent.

Geoaccumulation index averages, I_{geo}, are shown in Table 4. According to the Müller (1979) scale, Altata-Ensenada del Pabellón lagoon system is subject to pollutant effects, particularly with regard to Pb, which shows an average of $I_{geo}=2.6$ (*moderately* to *strongly polluted*) with 29% values falling into the *strongly polluted* class (>3). Cr, Ni, and Zn presented an average I_{geo} value corresponding to *unpolluted*, although there were some stations with data falling into the *moderately polluted* class, which are located mainly in the inner lagoons and the Ensenada del Pabellón region, near the sites where the agricultural effluents are discharged.

Sinex and Helz (1981) reported that EFs are generally not very sensitive to the choice of a baseline, while Covelli and Fontolan (1997) mentioned that the use of different

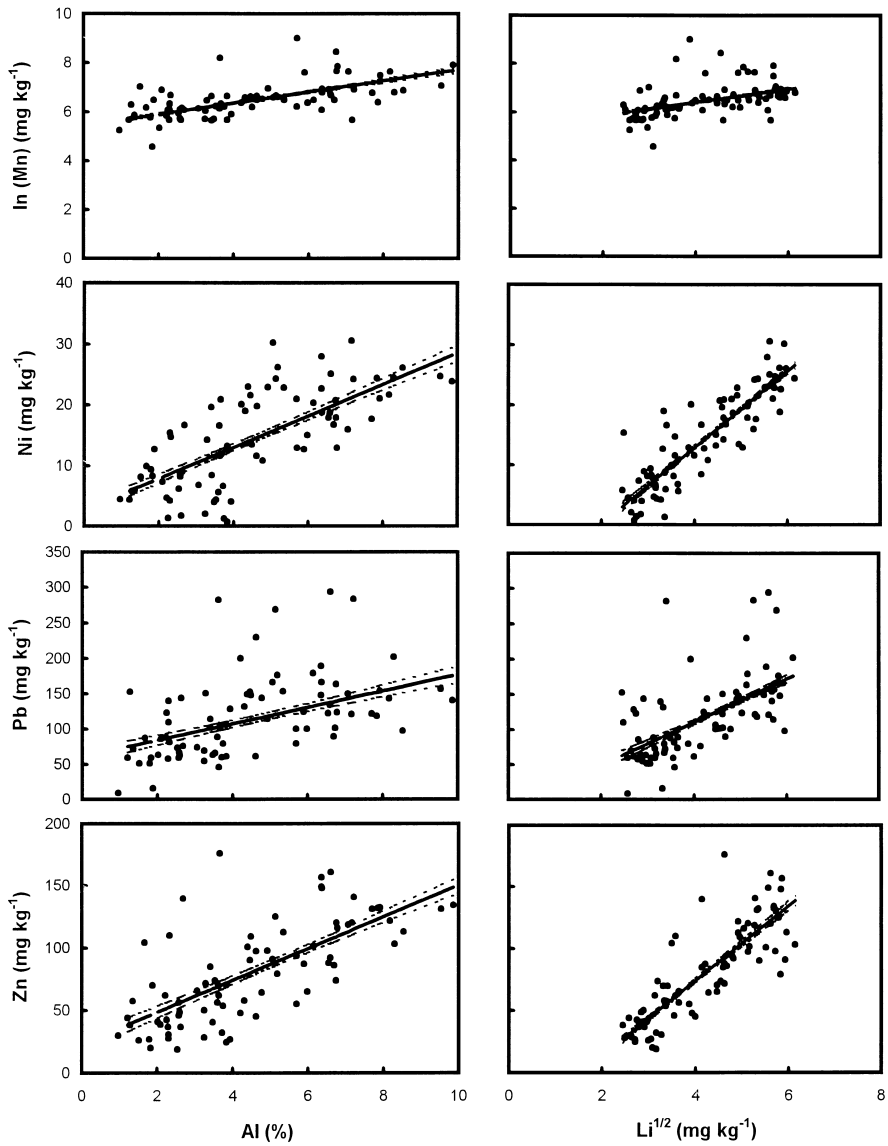

Fig. 5. Linear regressions for ln(Mn), Ni, Pb, and Zn concentrations as a function of Al (left) and $Li^{1/2}$ (right) concentrations. Plots show all points, including outliers that were omitted from the regression analysis. The regression line (solid) and 95% confidence band (dashed lines) according to Summers et al.'s (1996) criterion are shown.

metal values baseline has little influence in the classification according to I_{geo} classes. The Humaya and Tamazula sites were used as baselines in the EF and I_{geo}, however, the former showed enrichment with Cr when Szefer's method was employed, and with Co, Cr, Cu, Mn, Ni, and Zn using Summers' criteria. On the other hand, the highest EF values for Cr, Fe, and Pb in Station 69 were not detected as anomalous with Szefer's criteria and employing I_{geo} classes. This site was considered unpolluted when considering Cr and Fe results. This reveals the necessity to use more than one criterion to distinguish sites with anomalous levels of heavy metals. Highest I_{geo} values were consistent with anomalies detected by using Szefer's normalizing criteria with both Al and Li as conservative elements, while using Summers' criteria, anomalies detected involved the same stations with Szefer's criterion and a significant number of stations classified as unpolluted by I_{geo} criteria.

Table 4
Average values of EF and I_{geo}

Element	EF Al	EF Li	I_{geo}
Co	0.6	1.0	0.1
Cr	0.4	0.7	− 0.4
Cu	0.8	1.2	0.6
Fe	0.8	1.2	0.5
Mn	0.7	1.1	0.1
Ni	0.5	0.8	− 0.1
Pb	3.6	5.4	2.6
Zn	0.6	0.8	− 0.1

4. Conclusions

(1) A direct relation between stations considered to be enriched by Cr, Cu, Mn, and Pb, and agricultural discharge drains was observed.

(2) The data from EF and I_{geo} analysis indicate that Altata-Ensenada del Pabellón lagoon system is subject to pollution, particularly with regard to Pb.

(3) Correlation coefficients for relationships between metals and $Li^{1/2}$ and Al suggest that Li is a better normalizer than Al for granulometric variability when sediments from Altata-Ensenada del Pabellón coastal lagoon were analyzed.

(4) Summers' procedure (95% prediction intervals) was more rigorous than Szefer's strategy (regional anomalies), since the amount of polluted sites showed by Summers' criteria is considerably larger than that showed by Szefer's method.

(5) A general conclusion is that it is necessary to use more than one criterion to evidence sites with anomalous levels of heavy metals in coastal lagoon systems associated with intensive agriculture and suburban influence.

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