Bull. Environ. Contam. Toxicol. (2001) 67:741–748

DOI: 10.1007/s00128-001-0185-9

Bulletin of Environmental Contamination and Toxicology

Principal Component Analysis Applied to the Assessment of Metal Pollution from Urban Wastes in the Culiacán River Estuary

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Received: 1 April 2000/Accepted: 26 June 2001

Heavy metals and organic contaminants discharged into the aquatic environment have strong affinity for sedimentary particle surfaces. Therefore, by studying the sediments, it is possible to assess the scale of pollutant inputs into aquatic ecosystems from past industrial and urban development (Valette-Silver 1993); and depending on the geochemical tracer available, it is possible to identify the sources of those pollutants (DelValls et al. 1998). In this paper, geochemical carriers (organic carbon, Al, Fe, Li and Mn) and trace metals (Ag, Cd, Co, Cu, Ni, Pb and Zn) were analyzed in a sediment core to evaluate sewage pollution at Culiacan river estuary and factor analysis was used to assess the diverse sources and mechanisms influencing the metals distribution in sedimentary column of the estuary.

Culiacan river is located in the Pacific coastal plain province of Mexico. It has a drainage basin of 17,195 km^2 and 82 km of longitude until discharging in the Altata-Ensenada del Pabellon coastal lagoon system (AEP) (Fig. 1). Culiacan river is the most important perennial river in the region but currently, it is totally derived to irrigate the agriculture lands of Culiacan valley, which is a coastal plain that contains more than 130,000 ha of intensive agriculture where large amounts of fertilizers and pesticides are applied. The wastes of these agrochemicals drain toward AEP, either by runoff or through several drainage channels, some of them connected to the Culiacan river. After being derived, Culiacan river receives the sewage from Culiacan City and other surrounding settlements (about 855,000 inhabitants) at a rate of 160,206 m^3 d^{-1}, constituting in about the 21% of the Culiacan river total volume discharged.

MATERIALS AND METHODS

One sediment push-core (35 cm long) was taken by using a plastic tube (7 cm id) in November 1998, at the hypo-haline zone in the Culiacan River estuary. The core (RC98) was carefully subsectioned into 1 cm intervals and stored frozen (-20° C) until analysis. The samples were freeze-dried to constant weight, they were ground to a powder with an agate mortar and stored in plastic bottles.

Grain size analysis was done by using standard sieve and pipette methods (Galehouse 1971). Carbonate content was analyzed by using a colorimetric

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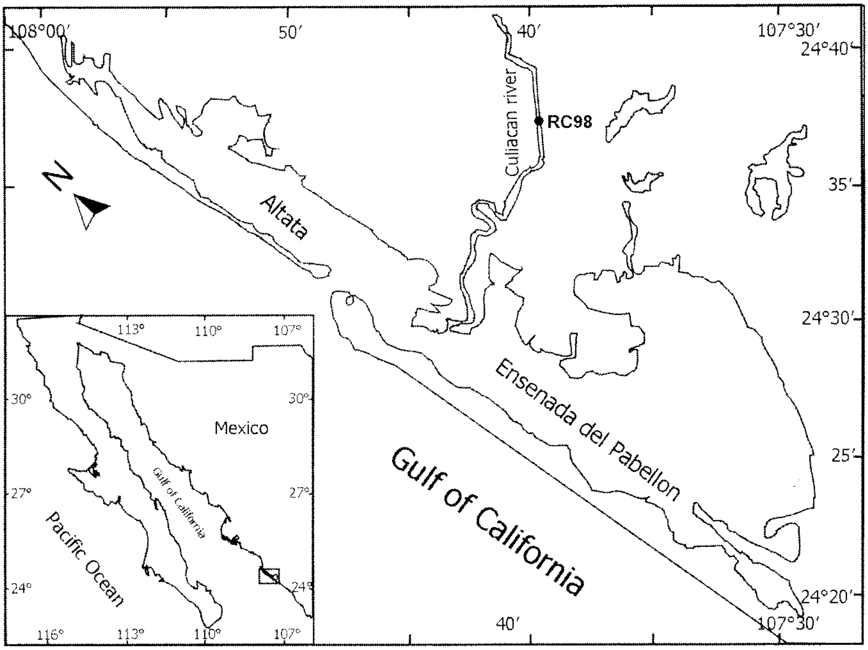

Figure 1. Location of sampling site in Culiacán river estuary (SE Gulf of California)

procedure in which the sediment sample was treated with HCl 1 N and the acid excess was titrated with NaOH 0.5 N (Stuardo & Villarroel 1976); and organic carbon content, by using a colorimetric procedure in which the sample was treated with an oxidant mixture of $K_2Cr_2O_7$ + Ag_2SO_4 + H_2SO_4 and the excess was titrated with $Fe(NH_4)_2(SO_4)_2$ (Loring & Rantala 1992). Sediments for metals and ^{210}Pb analysis were dissolved by acid digestion (1:1:0.5 HNO_3+HCl+HF) in closed Teflon®PFA containers (Loring & Rantala 1992). ^{210}Pb was determined by alpha counting of ^{210}Po deposited onto silver discs by using ^{209}Po as yield tracer (Flynn 1968); and metal analyses were done by atomic absorption spectrophotometry (AAS). Accuracy of the metal analyses was evaluated by using samples of standard reference materials (IAEA-300 and BCSS-1) and analytical precision by using six replicates of a homogenate sample. Recoveries (%) varied according to the metal, as follows: 100 for Ag, 89-101 for Al, 96-116 for Cd, 88-152 for Co, 93 for Cu, 81-104 for Fe, 53 for Li, 54-89 for Mn, 87-97 for Ni, 105-109 for Pb and 95-97 for Zn; and variation coefficients estimated were minor to 8%.

RESULTS AND DISCUSSION

Sediment core was characterized by an almost homogeneous content of sands (>90%) and rather low contents of organic carbon (OC) and carbonates (0.3-3.0% and 0.1-3.1%, respectively). The intervals of concentration found for the metals analyzed are listed in Table 1 and their profiles are presented in Fig. 2 (a-d). Fe and Mn profiles showed increasing trends toward the surface, with the highest contents of Mn and Fe at the oxic sediment-water interface. Al and Li contents showed rather small variations, indicating that sediments accumulated

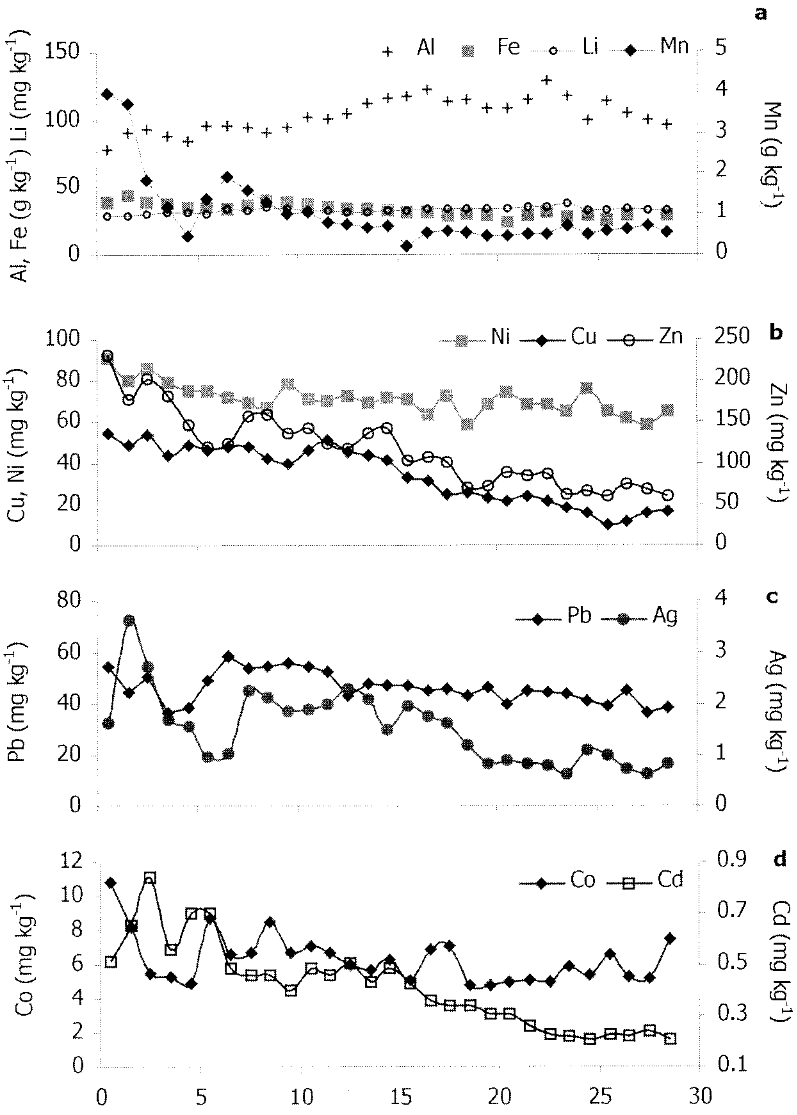

Figure 2. Trace metals profiles in core RC98.

within the core had a similar source; and Al and OC significant correlation (r^2=0.62) suggested that terrigenous input was the main source of the OC delivered to the sediment.

All the trace metal profiles showed a general increasing trend toward the top of the core, with a few highs and lows at various depths. Those trends may arise from a combination of either anthropogenic or natural causes; but if metals are not mobilized in the sediment by diagenetic reactions, the vertical changes allow a comparison of accumulation over time (Dickinson et al. 1996). The bottom layers having low concentration likely reflect the undisturbed and background concentration (metals supplied by clastic sources under natural conditions), while the upper layers that showed higher concentrations for all the metals reveal the increasing input of metals, likely due to anthropogenic activities. Natural variations in the concentrations related to grain size, organic carbon content changes or diagenetic mobility were neglected here, considering that grain size distribution and organic carbon were practically uniform within the core. Additionally, a final evidence to support the immobility of trace metals such as Pb is difference between ^{210}Pb and Pb profiles, since ^{210}Pb activities showed the greatest activities at surface as expected, and Pb concentrations showed subsurface maxima. The preservation of distinctly different profiles of ^{210}Pb and Pb in the core suggests that these metals are not being diagenetically mobilized (Cochran et al. 1998).

Al showed significant negative correlations with most of the trace metals analyzed, excepting Pb and Ag, indicating that observed enrichments are not result of increased clay content, but rather of a different provenance. OC content correlated significantly ($P \leq 0.05$) with the concentrations of Ag, Cd, Cu, Fe, Mn, Ni and Zn revealing that the organic matter sources are supplying also all those metals to sediments in nearly invariant proportions. The positive intercept found for each correlation (Table 1) has been interpreted as the natural metal content in the sediments, most likely fixed in the clays (Müller 1977). Relatively constant metal contents found at those depths where excess ^{210}Pb is not present (pre-industrial period), define the natural concentration levels (NCL) for the metals analyzed (Table 1). NCL's obtained from the metal profiles are quite similar to those values estimated from the relationship metal-OC, excepting for Mn. Natural Mn values found in the deepest layers of the core are around 3 times higher than those theoretical values, likely due to the diagenetic mobility of Mn.

A contamination factor (CF) was calculated for the sediment metal content. It was defined as the ratio between the metal concentrations found at a given horizon and the NCLs and this value reflects the metal enrichment in the sediment at that horizon. When $CF>1$ for a particular metal, it means that a contamination exists; otherwise, if $CF \leq 1$, there is no metal enrichment of natural or anthropogenic origin. For classification purposes, these CF's are divided into three categories of pollution (Soares et al. 1999): low (from CF's> 1 and up to 3; intermediate from 3 to 10; and high for CF's larger than 10. The CF's estimated for those metals analyzed in core RC98 are presented in Table 2. The highest contamination factors were found in Ag (> 4) and Cd, Cu and Zn ($\geq$ 3) while Co, Ni and Pb showed values smaller than 2. CF values obtained point out an intermediate pollution for Ag and a slight pollution for Cd, Co, Cu, Ni, Pb and Zn.

The increment of organic matter deposition to coastal waters has been related to intensive use of inorganic fertilizers, the population growth (Cornwell et al. 1996) and the increasing sewage inputs of particulate sedimentary matter (Stull et al. 1986). Therefore, enrichment in OC and trace metal found in the Culiacan river estuary, is likely related to the agriculture development, the increments in population and consequently in sewage load wasted from the urban settlements established around the Culiacan valley.

Table 1. Metal concentrations in sediment core RC98.

Metal*	**Ag**	**Al**	**Cd**	**Co**	**Cu**	**Fe**	**Li**	**Mn**	**Ni**	**Pb**	**Zn**
Interval	0.6-4	78-128	0.2-0.9	0.4-11	0.9-55	24-44	29-37	0.2-4	0.7-91	0.4-58	1-231
$[M^+]_{backg}$	0.9	116	0.2	5	18	28	35	161	64	43	62
NCL	0.9	110	0.2	5	18	28	34	555	66	42	72

$[M^+]_{backg}$ = Background metal concentrations (intercept of OC/M^+ relationship).
NCL= M^+ concentration found at the bottom of the sediment profile.
*Metal contents are given in mg kg^{-1} excepting for Al, Fe and Mn (g kg^{-1}).

Table 2. Contamination factors (CF) in sediments from core RC98.

Depth	**Al**	**Ag**	**Cd**	**Co**	**Cu**	**Fe**	**Li**	**Mn**	**Ni**	**Pb**	**Zn**
0.5	0.7	1.9	2.1	2.0	3.0	1.4	0.8	7.2	1.4	1.3	3.2
1.5	0.8	4.2	2.6	1.5	2.6	1.5	0.8	6.7	1.2	1.1	2.5
2.5	0.9	3.2	3.4	1.0	2.9	1.4	0.9	3.3	1.3	1.2	2.8
3.5	0.8	2.0	2.2	1.0	2.3	1.3	0.9	2.2	1.2	0.9	2.5
4.5	0.8	1.8	2.8	0.9	2.6	1.2	0.9	0.8	1.1	0.9	2.0
5.5	0.9	1.1	2.8	1.6	2.5	1.2	0.9	2.5	1.1	1.2	1.7
6.5	0.9	1.2	2.0	1.2	2.6	1.2	1.0	3.4	1.1	1.4	1.7
7.5	0.9	2.6	1.9	1.2	2.6	1.3	1.0	2.9	1.0	1.3	2.2
8.5	0.8	2.5	1.9	1.5	2.3	1.4	1.0	2.3	1.0	1.3	2.2
9.5	0.9	2.1	1.6	1.2	2.1	1.4	1.0	1.9	1.2	1.3	1.9
10.5	0.9	2.2	2.0	1.3	2.5	1.3	1.0	1.9	1.1	1.3	2.0
11.5	0.9	2.3	1.8	1.2	2.8	1.3	0.9	1.4	1.1	1.2	1.7
12.5	1.0	2.7	2.0	1.1	2.5	1.2	0.9	1.3	1.1	1.0	1.6
13.5	1.0	2.4	1.7	1.0	2.4	1.2	0.9	1.2	1.0	1.1	1.9
14.5	1.1	1.7	2.0	1.1	2.2	1.2	1.0	1.3	1.1	1.1	2.0
15.5	1.1	2.3	1.7	0.9	1.8	1.1	0.9	0.4	1.1	1.1	1.4
16.5	1.1	2.0	1.4	1.3	1.7	1.1	1.0	1.0	1.0	1.1	1.5
17.5	1.0	1.9	1.4	1.3	1.3	1.0	1.0	1.0	1.1	1.1	1.4
18.5	1.1	1.4	1.4	0.9	1.4	1.1	1.0	0.9	0.9	1.0	1.0
19.5	1.0	1.0	1.2	0.9	1.2	1.0	1.0	0.8	1.0	1.1	1.0
20.5	1.0	1.1	1.2	0.9	1.2	0.8	1.0	0.8	1.1	0.9	1.2
21.5	1.0	0.9	1.0	0.9	1.3	1.0	1.0	0.9	1.0	1.1	1.2
22.5	1.2	0.9	0.9	0.9	1.2	1.1	1.0	0.9	1.0	1.1	1.2
23.5	1.1	0.7	0.9	1.1	1.0	1.0	1.1	1.0	1.0	1.0	0.9
24.5	0.9	1.0	0.8	1.0	0.9	1.0	1.0	0.9	1.1	1.0	0.9
25.5	1.0	1.0	0.9	1.0	0.6	0.9	1.0	1.1	1.0	0.9	0.8
26.5	1.0	0.9	0.9	1.0	0.6	1.0	1.0	1.1	0.9	1.1	1.0
27.5	0.9	0.7	1.0	0.9	0.9	1.0	1.0	1.0	0.9	0.9	0.9
28.5	0.9	0.9	0.8	1.0	0.9	1.0	1.0	1.0	1.0	0.9	0.8

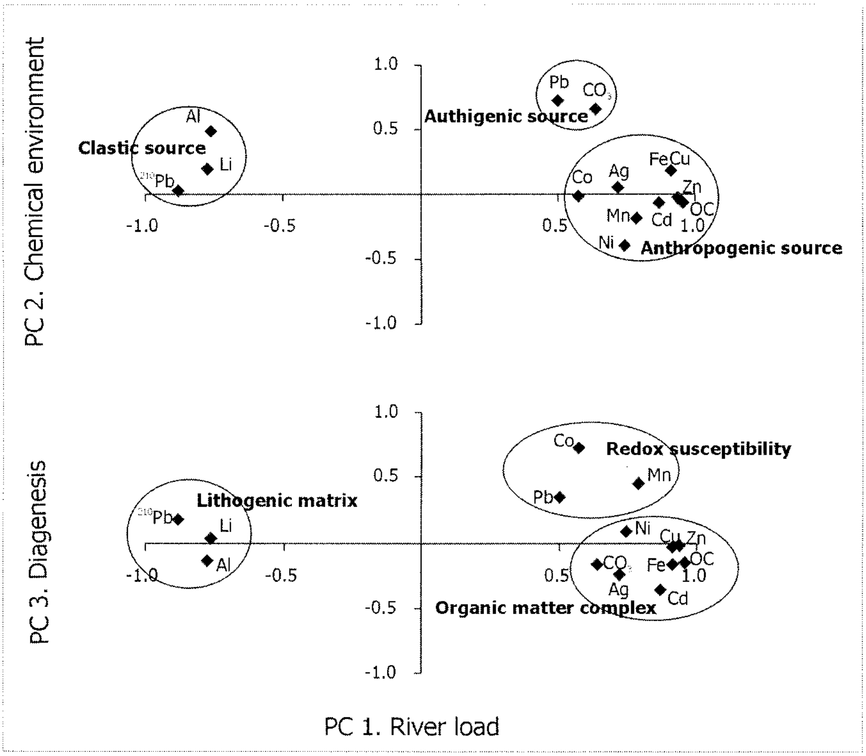

Figure 3. Scatterplots of PCA loadings by individual variables.

Factor analysis is a technique commonly used to analyze geochemical matrices by creating one or more factors, each representing a cluster of interrelated variables within the data set (DelValls et al. 1998). The factor loadings are related to the input provided by individual variables to a given factor and the variables that most strongly load a particular factor can be used to assign the physical meaning of this factor (Szefer & Kaliszan 1993). Principal component analysis (PCA) extracted three factors (eigenvalue >1) that accounted for more than 82% of the total variance from the 14 variables included in the data set (Fig. 3), and they are:

Factor 1 (River load) explains more than 63% of the variance. It includes OC, Ag, Al, Cd, Cu, Fe, Li, Ni, Mn, Zn and ^{210}Pb, as these components are almost certainly associated to the eroding soil of the watershed carried to the surface of the estuarine bottom while suspended in runoff, which includes also material accumulating from the atmosphere (as ^{210}Pb), particulate and particulate material either of anthropogenic (fertilizers and pesticides used in agriculture, as well as domestic wastes) or geochemical weathering origin. High loadings on OC and Ag suggest a contamination source associated with untreated urban wastes into the Culiacan River estuary and the increasing concentrations of metals detected in the sediments from the CF's showed the impact that this sewage input has had during the last decades.

Factor 2 (Chemical environment) accounts for almost 11% of the variance. Pb and carbonates (CO_3) are grouped under this factor indicating that a high proportion of lead in sediments appears to be associated with the carbonates. This suggests that pH in the environment is inducing the appropriate conditions to promote the precipitation of Pb likely as cerussite ($PbCO_3$), instead of being adsorpted onto Fe/Mn oxides, as noted elsewhere (Gee et al. 1997, Maskal & Thornton 1998).

Factor 3 (Diagenesis) explains more than 10% of the variance and includes Co and Mn. This is attributed to a postdepositional diagenetic vertical redistribution caused by remobilization and reprecipitation of Co on Mn oxyhydroxides coatings, along the core analyzed, because of Mn redox properties.

Distribution of principal components loadings form three clearly isolated clusters. The values of the loadings on the vector 1 distinctly differentiate Ag, Cd, Co, Cu, Fe, Mn, Ni, Zn and OC, (positive values) from Pb and CO_3 and from Li, Al and ^{210}Pb (negative values). Considering that Al and Li are index elements of crustal origin, OC and Ag are related to the allocthonous organic matter (sewage) and CO_3 is the result of in situ primary production, the three loading clusters have discriminated adequately the metal provenance for terrigenous (Li, Al and ^{210}Pb), authigenic (Pb and CO_3) and anthropogenic sources (OC, Ag, Cd, Co, Cu, Fe, Ni, Pb and Zn).

Acknowledgments. Thanks are due to G Ramírez-Reséndiz and MC Ramírez-Jáuregui for assisting in the preparation of the manuscript. Financial support was provided by UNAM-DGAPA, the Organization of American States (OAS) and the grant CONACyT 27953T.

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