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Principal Component Analysis of Dissolved Heavy Metals in Water of the Reconquista River (Buenos Aires, Argentina)

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It is well known that the use of hydric basins as receptors of anthropogenic unloadings represents a risk to human health. Particularly important is the contamination provoked by high concentration of heavy metals being their adverse effects increased by persistence and biomagnification phenomena. Heavy metals enter the aquatic environment mainly by direct discharges from industrial sources (Nriagu 1988).

The Reconquista river belongs to the larger watershed of the River Plate, the most important source of freshwater for Buenos Aires city and the surrounding urban area. It receives several tributary streams, being the more important the Moron creek. Approximately 10% of the total country population and some 10000 industries occur in its flood plain thus deteriorating the quality of water by the sustained urban and industrial discharges. In a previous series of papers, we reported the evaluation of the water quality of the river and determined its pollution degree (Castañé et al. 1998 a, 1998 b; Topalián et al. in press).

Principal components analysis (PCA) is a useful tool in the examination of multivariate data (Zitko 1994). In the present work, we used PCA to evaluate an aspect of the impact of human activity on the Reconquista river, focusing on the quality of the surface water through the measurement of dissolved As, Cd, Cu, Cr, Pb and Zn concentrations at three sites during two years, which is so far the longest monitoring carried out on the Reconquista river.

MATERIALS AND METHODS

The Reconquista river is situated in a subtropical region. It is characterized by a low flow (69000 to 1700000 m3/day). Its width varies from 4 - 14 m in Cascallares (S_1) and up to 20 - 25 m in Bancalari (S_3); its depth is 0.5 - 1.0 m in Cascallares and approximately 2.0 - 2.5 m in Bancalari (Figure 1).

Duplicate surface water samples were collected monthly at three locations from February 1994 to February 1996. Site 1 (S_1): Cascallares, is located at 5 km of the mouth. Site 2 (S_2): San Martin, is located 38 km from the mouth in an urban and

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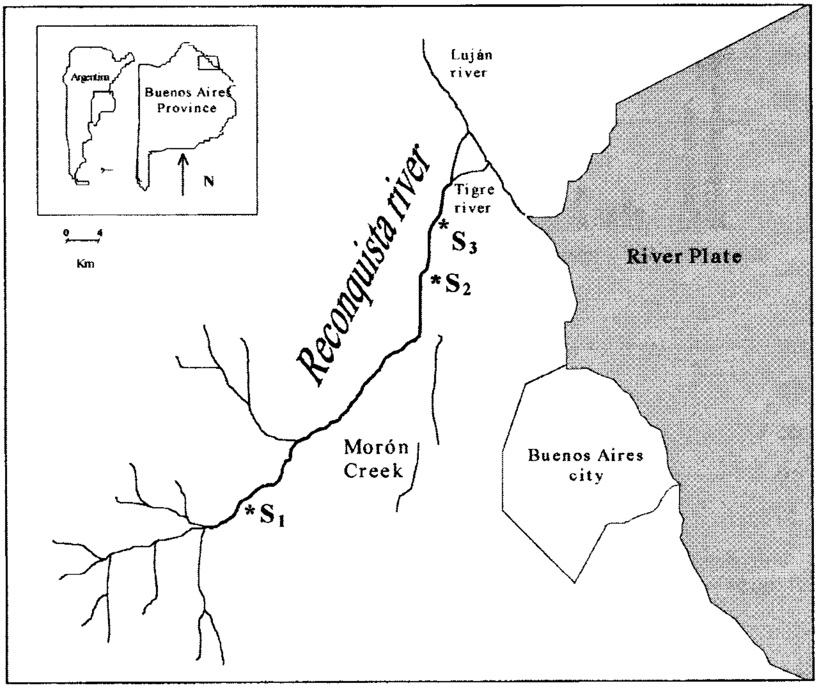

Figure 1. Geographic location of Reconquista river and sampling sites.

industrial zone, after the Moron creek which contributes with an important pollutant flow. Site 3 (S_3): Bancalari, is located at 46 km in an industrial zone, up the tidally-influenced zone. A considerable part of the margins between S_2 and S_3 is used as a metropolitan garbage filling area.

Water samples were filtered (0.45 µm pore) and acidified with HNO_3 to pH < 2, according to the technique from Standard Methods for the Examination of Water and Wastewaters (APHA 1992). Samples were analysed by atomic absorption spectrometry (Shimadzu AA 6501) with a graphite furnace atomizer (Shimadzu GFA 6000). The detection limits were (in $\mu g.L^{-1}$): As - Pb = 5; Cr - Cu = 2 and Cd - Zn = 1. Values obtained were compared with the maximum permissible quantities (MPQ) established by the Argentine Dangerous Wastes Law (N° 24051) for protection of freshwater life, considering a hardness range between 120-l80 mg $CaCO_3.L^{-1}$ as it was measured in most of the samples.

For the PCA analysis, data were adjusted to a normal distribution with the transformation $sen^{-1}/1000$. The analysis was based on the correlation matrix following the method described in Legèndre and Legèndre (1979). A fiducial significance level of $p < 0.05$ was chosen.

RESULTS AND DISCUSSION

Figures 2 and 3 show metal concentrations along the sampling period, as well as

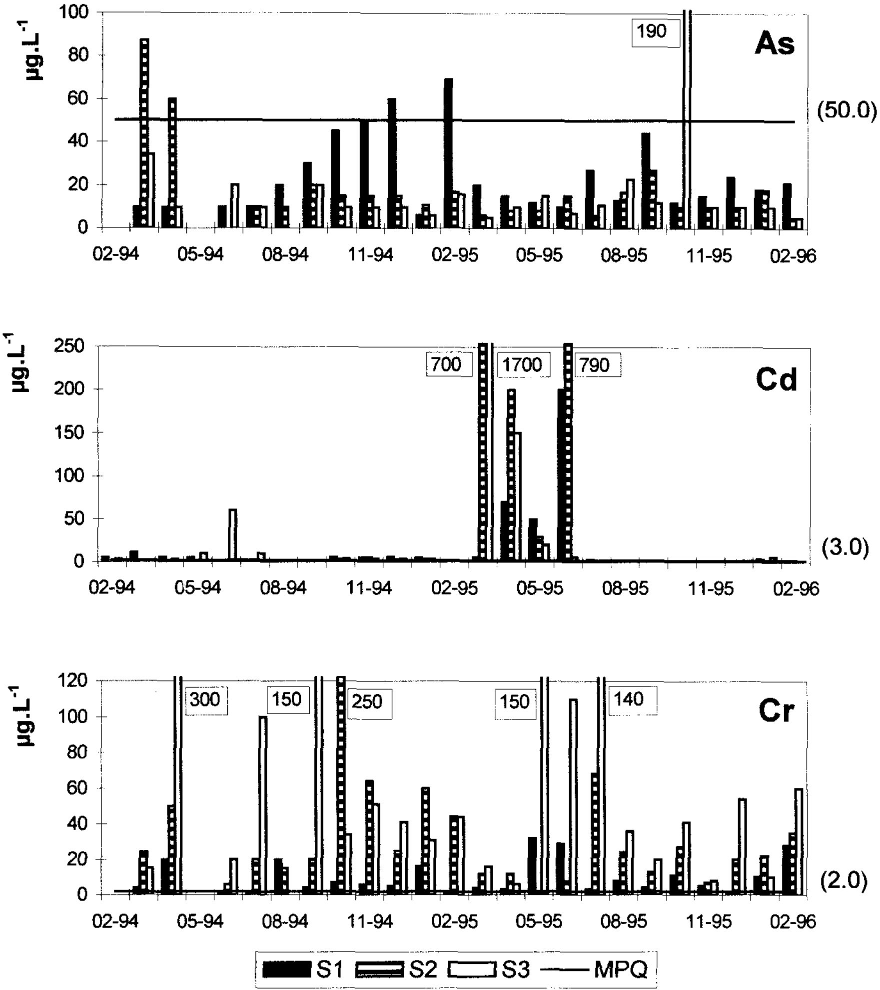

Figure 2. Concentration of dissolved As, Cd and Cr in the superficial water of the Reconquista river. In parenthesis, MPQ values.

the corresponding MPQs. Most values resulted higher than the MPQ, being the more dramatic differences found for Cr and Cu and, in a lower magnitude, for Pb and Zn.

PCA of the 74 x 6 matrix (74 samples and 6 metals) is presented in Figures 4 y 5. Figure 4 shows the plot of loadings which indicates relationship among variables. The first two principal components accounted for 54 % of the total variance (33 and 21%, respectively). In the first component (eigenvalue= 1.97), the greater contribution was due to the Pb (coef. 0.761), Zn (coef. 0.749) and Cu (coef. 0.727), with a positive correlation. The second component (eigenvalue = 1.27) presented a positive correlation with Cd (coef. 0.712) and negative with As (coef. - 0.651). Figure 5 A shows the plot of the samples scores identified by season. An examination of the position of the samples in the coordinates of the first two

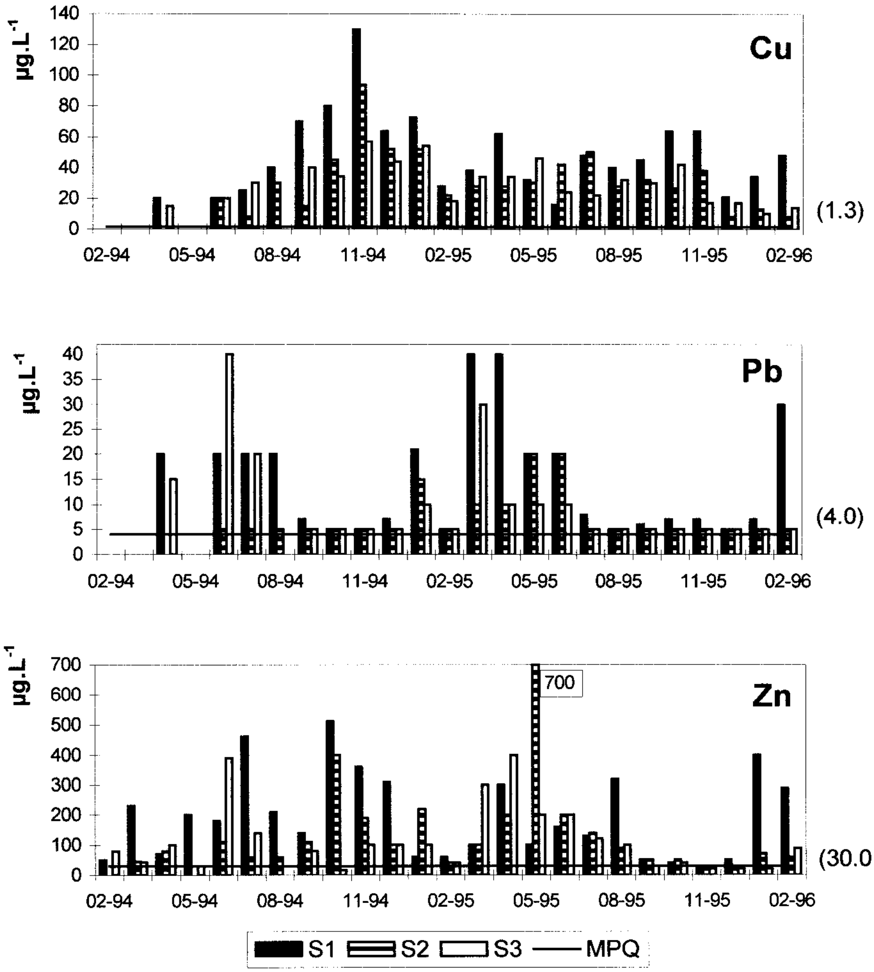

Figure 3. Concentration of dissolved Cu, Pb and Zn in the superficial water of the Reconquista river. In parenthesis, MPQ values.

principal components indicates that, along the second component, most of the spring and summer samples are settled in the lower part of the plot (with high As) and those of autumn and winter at the upper extreme (with high Cd). Figure 5 B identifies samples according to the sampling station. It cannot be observed any ordination which could suggest a spatial gradient. The results demonstrated that the Reconquista river suffers a high degree of deterioration in the water quality. Throughout the period of the present study, concentration values exceeded widely the MPQs for protection of aquatic life, being As 4 times, Cd 40000, Cr 150, Cu 65 and Zn 23 times higher than those limits.

An association among Pb, Zn and Cu was observed; it resulted independent of both season and sampling station. The lack of a relationship between values and sampling dates and sites suggests that heavy metals were poured permanently and

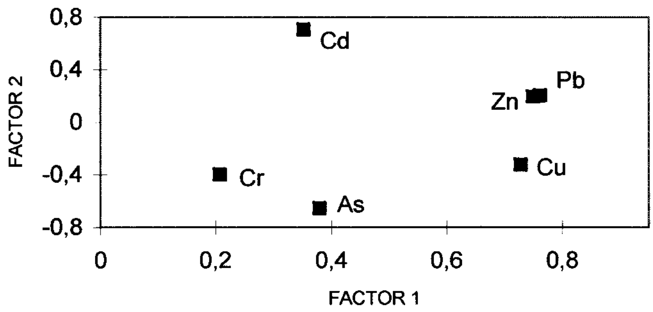

Figure 4. Plot of loadings of the first two principal components

randomly along the river, keeping their concentrations always higher than the MFQs.

It is worth mentioning that within the week previous to the samplings in January, March and December 1994, as well as in November 1995, heavy rains occurred (40 - 63 mm). However, consistent changes in heavy metals concentrations were not observed after those rainfalls.

It is known that particle reactive metals released to water are likely to accumulate in sediments (Ingersoll 1995). Seasonal variation in water temperature observed in the Reconquista river (Castañé et al. 1998) may have led to temporal variability in the flux of metals from the sediments, acting as a removal factor of heavy metal contaminants to the overlying water column.

Wachs has proposed recently (1998) an ecological classification of riverine systems based on the concentration of dissolved heavy metals; according to that classification, a water body excessively polluted (grade IV) shows the following concentration (in $\mu g.L^{-1}$): Cd >2, Cr >8, Cu >20, Pb >15 and Zn >140. In the Reconquista river, we report that those limits were exceeded in most cases: 47% of the samples showed higher levels of Cd, 64% of Cr and Cu, 20% of Pb and 32% of Zn. In spite of the fact that the River Plate has a considerably high capacity of dilution of the pollutants poured by the Reconquista river due to its large dimensions, Villar et al. (1997) determined values higher than the MPQs for Cd, Zn, Pb and Cr concentrations at a site located shortly downstream of the outlet of the Reconquista river. Comparing those values with our S_3 site, we observed that Cd mean concentration was 40 times greater than in the River Plate, Zn and Cr were similar, while Pb was 5 times lower. Kreimer et al. (1996) showed that the concentration of heavy metals in the sediments of coastal areas of the River Plate were very high.

Finally, our results point out the potential risk for the residents of the Buenos Aires city whose main source of drinking water comes from the River Plate which is the final recipient of the highly polluted water of the Reconquista river.

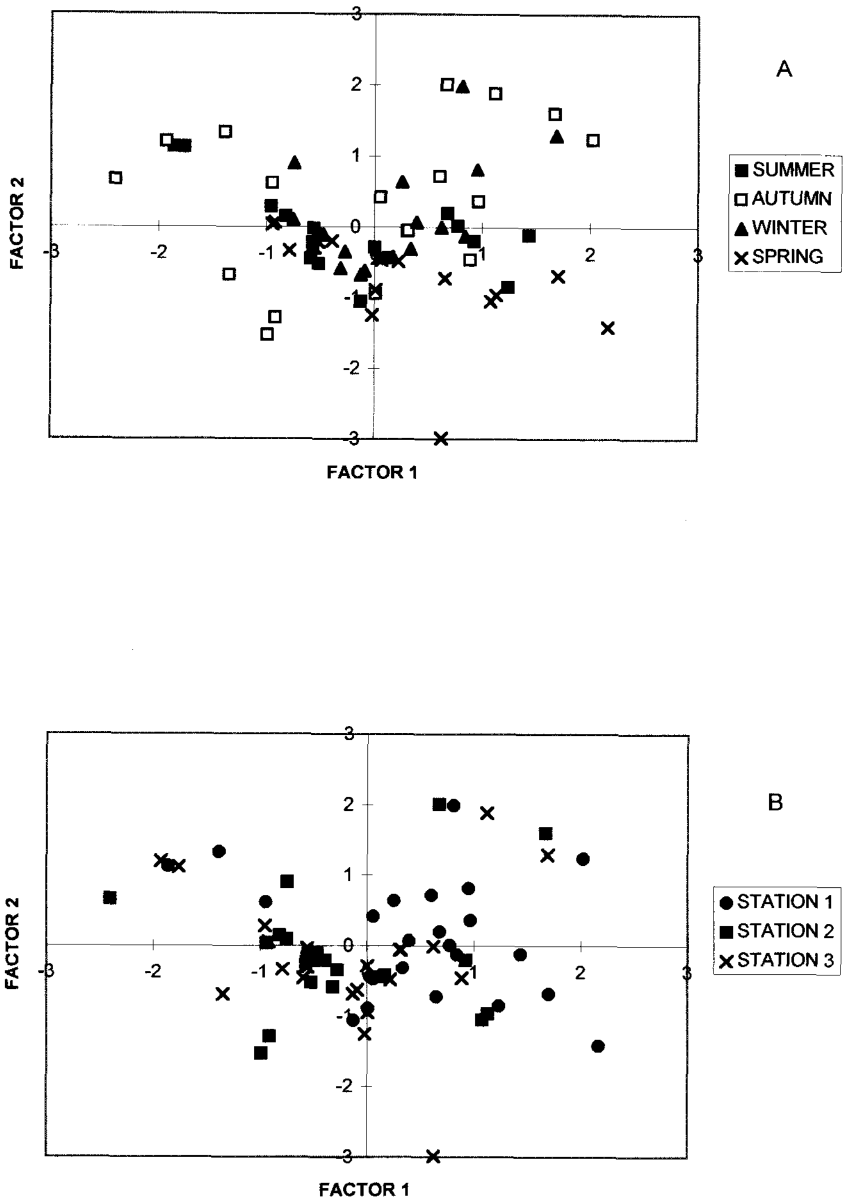

Figure 5: PCA Analysis: plot of sample scores of the first two principal components identified by A) season, B) sampling station.

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