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Evaluation of natural and anthropogenic influences on the Guadalquivir River (Spain) by dissolved heavy metals and nutrients

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Abstract

To evaluate both the natural and anthropogenic influences on surface waters of Guadalquivir River (SW-Spain), concentrations of dissolved trace metals (Mn, Co, Ni, Cu, Cd, Zn, and Pb), inorganic nutrients (N-NH_4^+, N-NO_3^-, N-NO_2^-, and P-PO_4^{3-}) and other variables as conductivity, pH, dissolved oxygen (DO) and suspended solids (SS) were measured during a three-years period (2001–2003). Samples were taken at 26 stations twice a year, during rain and dry periods. The analysis of variance (ANOVA) suggested that temporal variations within the period of study were statistically negligible. Spatial distributions identified three different zones, mainly influenced by sewage (Eastern Zone), agriculture runoffs (Central Zone), and estuarine processes (Western Zone), respectively. Principal Component and Cluster Analysis allowed to identify the variables controlling the water quality of each zone as: N-NH_4^+, N-NO_2^-, Mn, and Co, (Eastern Zone), SS, and P-PO_4^{3-} (Central Zone), and Cd, pH and conductivity (Western Zone). Other variables such as Ni, Cu, Zn or N-NO_3^-, influenced two different zones, while Pb presented a singular behavior.

Keywords: Heavy metals; Guadalquivir River; Water pollution; Estuarine water; Chemometric tools; Multivariate analysis

1. Introduction

Human activities are continuously modifying the quality of continental waters. Thus, in addition to a major source of suspended solids and inorganic nutrients (phosphates and nitrates), agriculture has been identified as a source of heavy metals via fertilizers (Giuffré de López Camelo et al., 1997; Moreau et al., 1998; Laws, 2000; Michel et al., 2000; Bashour et al., 2004; Micó et al., 2006; Kidd et al., 2007). Industrial effluents contain a wide variety of pollutants depending of the activities and, in many cases, high concentrations of trace metals have been reported (Ramos et al., 1999; Iribar et al., 2000; Terrés-Martos et al., 2002). Finally, trace metal concentrations in water may be also affected by municipal sewage effluents (Sorme and Lagerkvist, 2002; Karvelas et al., 2003; Al Enezi et al., 2004; Buzier et al., 2006).

Guadalquivir River is among the major freshwater sources of the European Atlantic basin. Despite its importance, there is only one peer-reviewed article that reports concentrations of dissolved trace metals (Mn and Cu) in Guadalquivir River (Mendiguchía et al., 2004). After the spill of toxic metals from the Aznalcóllar pyrite mine (April 1998) several articles were published, but they mainly focus on concentrations of Zn, Cu, Cd and Pb in organisms and sediments in the estuarine zone (Riba et al., 2002; Garcia-Luque et al., 2003; Martin-Diaz et al., 2005; Olías et al., 2006). The impact of this accident in the Guadalquivir River was mainly located in the zone closer to the Guadiamar River, but the concentrations of dissolved heavy metals recovered their original levels six months after the accident (Achterberg et al., 1999).

In a previous work, we performed a preliminary study to evaluate the water quality of Guadalquivir River based on

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nutrients and Cu and Mn concentrations (Mendiguchía et al., 2004). Now, for a better characterization of the inputs received by river water, we present a full study, extended in time, and based on concentrations of both nutrients and dissolved trace elements (Mn, Co, Ni, Cu, Cd, Zn, and Pb) as well as other variables such as DO or conductivity. Some of the data previously reported have been used for statistical treatments.

1.1. Description of the area of study

The Guadalquivir is Spain's second longest river, and it is among major European rivers. With a length of 657 km, it flows southwest through the region of Andalusia, with a drainage area of 57 527 km^2, affecting population of more than 4 millions inhabitants, and passing Cordoba and Seville as major cities. Its natural environment is one of the most varied in Europe, containing representatives of half of the continent's plant species and nearly all those of the North African region. The fauna also includes a great variety of European and North African species (UNEP, 2004).

The lower course traverses extensive marshlands that are used for rice cultivation. The river is tidal to Seville (about 90 km upstream), a major inland port and head of navigation for ocean-going vessels. Navigation up to the Port of Seville also leads to a serious environmental problem due to erosion and pollution.

In this work we studied the navigable part of the Guadalquivir River, from the mouth to Alcalá del Río, where a dam controls the flow of the river. At the investigated section, with a length of about 115 km, the river flows in direction Northeast–Southwest. Along its course, about 20 km downstream the starting point of the study, the river passes through Seville, with a population of more than 700 000 inhabitants. It is the main urban and industrial centre of the zone. Its industrial and domestic wastewaters are treated before discharging into the river. The four sewage treatment plants with secondary depuration systems have a total treatment capacity of 445 000 m^3 d^{-1} (Figure S1, Supplementary material).

While other small villages may be found, the main activity carried out between Seville and the estuary is agriculture and related industries. The estuary has an added ecological value due to the presence of the Doñana National Park, an important and protected wetland area.

2. Materials and methods

2.1. Sampling

Between the years 2001 and 2003, up to 6 sampling campaigns were conducted abroad the AMA V of the Andalusia's Environmental Authority. Three of these expeditions were carried out during rain periods (March 2001, March 2002 and April 2003) and the other three during dry periods (October 2001, October 2002 and November 2003). Maximum tidal height in the river is about 1.8–3.6 m. A description of tidal situation during sampling campaigns may be found in (Figure S2 Supplementary material). Although heavy rains could modify water characteristics, the water flow of the river is controlled by the dam. During sampling campaigns the average flows were (chronologically): 270, 51, 15, 27, 35 and 39 m^3 s^{-1}. Samples were collected at 26 stations chosen by two different criteria. In the upper part of the river, 13 stations (G1–G13) were selected using geographical consideration and taking into account the activities developed in the basin. In the estuary (stations G14–G26) samples were collected to cover the whole salinity range.

Three different samples were collected at each point, to analyze suspended solids, nutrients, and metals, respectively. Except to those used for suspended solids, the samples were filtered on-line through 0.45-μm pore-size acid-washed polypropylene Calyx Capsule (Osmonics, USA).

To provide reliable and accurate trace metal data, clean techniques were used for handling and analyzing samples. All material coming in contact with the samples was acid washed and stored in double polyethylene bags until required. The samples for dissolved traces metals were acidified with high-purity HNO_3 (Suprapur, Merck, Germany) in a class 100 laminar flow bench located into a class 10 000 Clean Room, stored for three months and then analyzed.

2.2. Analytical procedures

An electrochemical portable device (Sension 156, Hach Co., USA) was used for in situ measurements of temperature, pH, DO and conductivity/salinity. Suspended solids were gravimetrically quantified by using 0.45-μm nylon filters (Osmonics, USA). To analyze nutrients, spectrophotometric standard methods were applied (Grasshof et al., 1983; Tovar et al., 2001, 2002). Cu and Mn were determined by the standard addition method in a flameless atomic absorption spectrometer (Model SolaarM, Thermo Electron, USA), employing Zeeman correction. For the determination of Co, Ni, Zn, Cd, and Pb, samples were pre-concentrated in the Clean Room facilities by solvent extraction with ammonium 1-pyrrolidine-dithiocarbamate/diethylammonium-diethyldithiocarbamate (APDC/DDDC) (Bruland and Frank, 1983), and then quantified on a Series X7 (Thermo Electron, USA) inductively coupled plasma mass spectrometer (ICP-MS), employing ^{89}Y and ^{209}Bi as internal standards.

Analytical procedures were verified by analysing two certified reference materials (LGC-6010 and SPS-SW2). All trace elements gave both accurate and precise results, with relative errors between −0.8% (Pb) and +8.4% (Cd) and relative standard deviations between 0.7% (Zn, $n = 4$) and 14.3% (Cu, $n = 3$).

2.3. Statistical procedures

Two-way ANOVA was performed in order to establish the existence of temporal and spatial differences between water samples from Guadalquivir River. Previously, normality and homogeneity of data were checked by means of the Kolmogorov-Smirnov and Levene tests, respectively. Logarithmic transformations were performed for SS and Zn, and cube root for Mn. For not homogeneous or not normal distributed variables (N-NO_3^-, N-NO_2^-, N-NH_4^+, PO_4^{3-}, and Pb) the non-parametric Kruskal-Wallis' test (K–W) was used (Miller and Miller, 2005; Zar, 1998).

To assess relationships between variables and possible patterns in the distribution of the measured data, we used Principal Component Analysis (PCA) and hierarchical Cluster Analysis (CA), using SPSS for Windows 11.0.1 (SPSS Inc., USA). PCA was applied to obtain composite variables providing information about the existence of patterns and on the meaning of latent factors responsible of these patterns. Eigenvalues and varimax rotation mode were used to extract and represent principal components (PCs), which are then also called varifactors. CA was performed to identify any analogous behavior between the different sampling stations or between the measured variables. Dendograms were constructed using the squared Euclidean distance between normalized data in order to measure similarity between samples, and both average linkage between groups and Ward's method to establish different clusters.

3. Results and discussion

The results from ANOVA and K–W suggested the absence of significant temporal differences, between the data obtained in the different sampling campaigns. This fact may be explained because of the small flow variations between sampling campaigns due to the dam-controlled water flow. Measured data are reported in (Table S1 Supplementary material). Thus, average values were calculated for each station, represented in form of box-whiskers plots, and included in different figures for physico-chemical variables (Fig. 1), nutrients (Fig. 2) and metals (Figs. 3 and 4).

3.1. Physico-chemical variables

Although all the sampling stations were located in the zone of tidal influence, the variations in conductivity were observed only between G13 and G26 (see Fig. 1). For each sampling expedition, depending on the river flow and tidal situation, the increase of conductivity was located between stations G13–G16, closer to G13 with rising tide and to G16 with ebb tide.

The lowest values of pH and DO were found near to Seville, between G6 and G10, where main sewage inputs were located, introducing acidic effluents with higher content of organic matter, which is degraded by bacteria, utilizing DO in the process. Further on, both pH and DO increase due to seawater input to the estuary.

The results of SS for the last sampling expedition were much higher (up to 10–15 times) than those obtained for previous campaigns, due to the very high precipitations. Thus, they were not included in Fig. 1. Maximum of SS concentrations appeared between G9 and G13, with a mean of about 200 mg l^{-1}, corresponding to the agricultural zone, with extensive areas devoted to rice cultivation and the beginning of the estuarine mixing zone, which acts as a trap for particulate matter (Zwolsman et al., 1997; Dassenakis et al., 1997). In the estuary this variable presented an opposite behavior than pH and DO, decreasing its concentration as water salinity increased due to dilution effect.

3.2. Nutrients

Both ammonium and nitrites presented a maximum in the urban zone (G5–G8), with concentrations about three times higher than in the previous zone, and originated by sewage effluents and nitrification processes, respectively. Similar behavior was previously reported in River Kennet, UK (Neal et al., 2000). Very high concentrations of nitrate (up to 11.02 mg l^{-1}) were found in a wide area of the river, especially between G1 and G13. In fact, nitrate was the only variable that exceeded the critical value (1400 μg l^{-1}) established by local authorities. In this case, the profile obtained cannot be explained with a single source. Thus, in addition to the increase of nitrate concentration from nitrification processes in the urban zone, the high concentrations of nitrate obtained in G1–G3 and G10–G13 should be associated to other sources, such as agriculture.

The trend observed for phosphate was similar to that for suspended solids, with maximum concentrations in the intermediate zone, corresponding to extensive agricultural zones to as previously reported for Ganga River, India (Jain, 2002). In our case, phosphate fertilizers are probably used in an area which is mostly devoted to a flood-irrigated rice culture, discharging large amounts of solids to the river. Thus, phosphate and suspended solids do not present necessarily a chemical relationship but a shared origin.

3.3. Metals

In general, the concentrations of dissolved metals are close to the values reported for other rivers in Europe (Table 1). The curves for Mn and Co were very similar to ammonium, with high concentrations near sewage effluents, although cobalt showed also a maximum in G1 as nitrate. The presence of high concentrations of Mn and Co in wastewater and in rivers affected by sewage effluents was previously reported (Karvelas et al., 2003; Markich and Brown, 1998; Buzier et al., 2006).

Highest concentrations of Ni were measured between G9 and G13, where agriculture is the predominant activity.

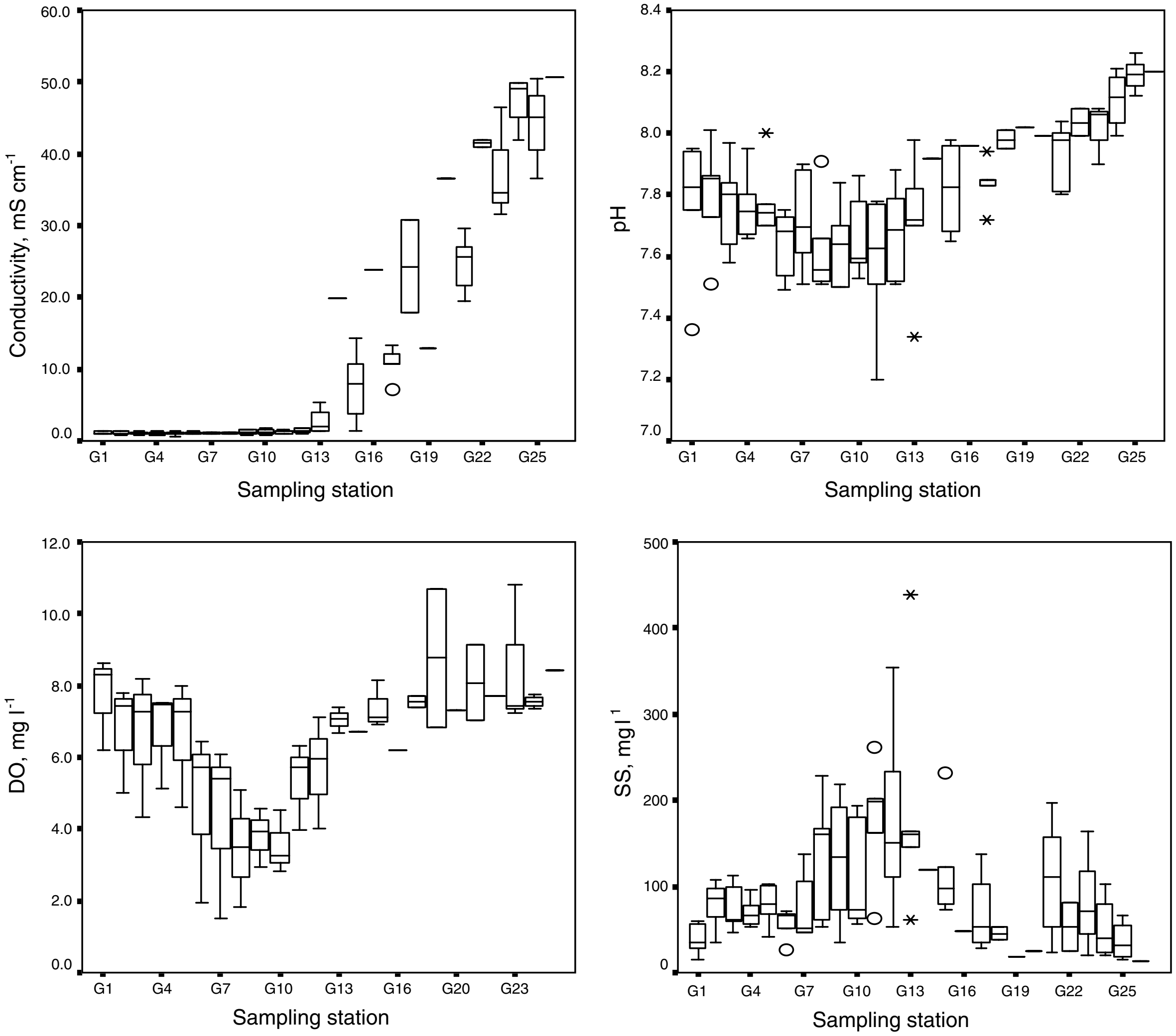

Fig. 1. Spatial variations of conductivity, pH, dissolved oxygen and suspended solids in the sampling stations of Guadalquivir River. ○ and ∗ denote outliers with 1.5 × IQR and 3 × IQR, respectively (IQR: Interquartile range).

Although some authors have associated the increase of Ni in rivers with sewage effluents, the concentrations were about 0.3 μg l^{-1}, 10-times lower than our results (Markich and Brown, 1998; Dassenakis et al., 1998). The concentrations measured in the Guadalquivir River (over 3 μg l^{-1}), are in better agreement with the results reported for agriculture zones, i.e. 1.46 μg l^{-1} in Acheloos River, Greece (Dassenakis et al., 1997) and 8.00 μg l^{-1} in Mekong River, Vietnam (Cenci and Martin, 2004).

Cu profiles presented maximum concentrations in the middle zone suggesting also an agricultural origin, as previously reported in other Spanish river (Linde et al., 1995). As observed in Fig. 3, concentrations of Cu and Ni decreased along the estuary due its lower concentration in seawater. This behavior identifies Guadalquivir River as a source of both metals to Atlantic Ocean, as also suggested, in the case of Cu, by Garcia-Luque et al. (2003).

The measured concentrations of Zn, Cd and Pb presented different profiles (see Fig. 4), suggesting different origins. The concentrations of Zn increased along the middle part of the river, although high concentrations were also found in G1, as observed for NO_3^- and Co, and lower in G25 and G26 due to the entrance of seawater from the Gulf of Cádiz, containing about 1.56–3.14 μg l^{-1} (Elbaz-Poulichet et al., 2001). Cd presented a profile similar to conductivity, suggesting again the importance of the input of seawater, with Cd concentration up to 5.62 nmol kg^{-1} (Elbaz-Poulichet et al., 2001), and also the partial remobilization from particles by changes in salinity, which, in the case of cadmium, has been described to be significant in different conditions (Standring et al., 2002). Finally, Pb showed an irregular trend, with concentrations lower that those reported in other similar studies, such as Hawkesbury-Nepean River, Australia (Markich and Brown, 1998) or in Acheloos River, Greece (Dassenakis et al., 1997). In general, highest concentrations mostly appeared in the intermediate zone, near agriculture areas. Some very high concentrations of Pb were measured in estuarine samples (some of them, even above 1 μg l^{-1}, were not included in Fig. 4). This anomaly was also observed for other

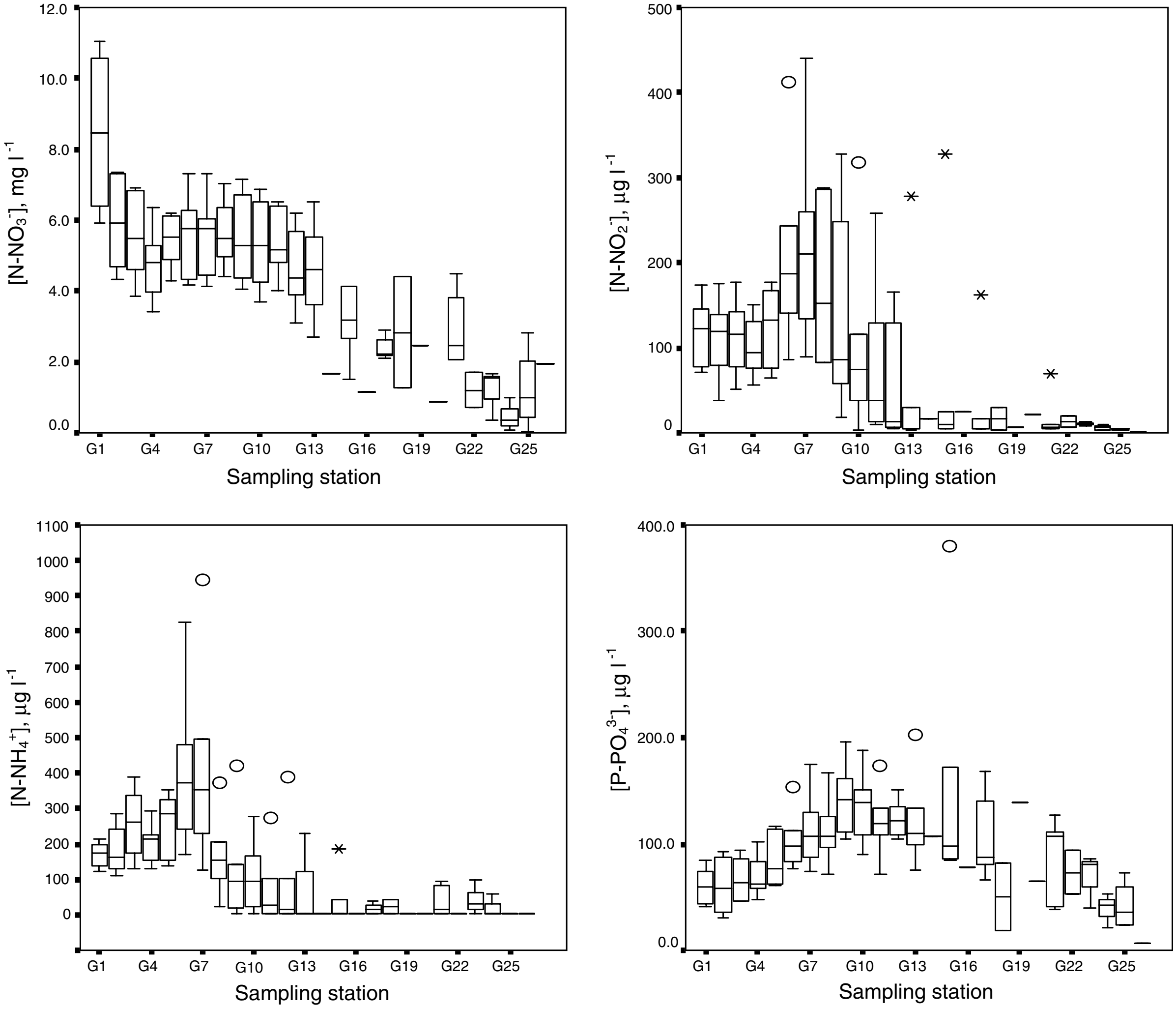

Fig. 2. Spatial variations of nitrate, nitrite, ammonium and phosphate in the sampling stations of Guadalquivir River. ○ and * denote outliers with 1.5 × IQR and 3 × IQR, respectively.

variables (PO_4^{3-}, Cu, Mn, Co, and Ni) although not at so high concentrations.

3.4. Principal component analysis

This analysis was carried out in order to reveal the data structure and eliminate redundant information. We obtained three principal components (PCs) with eigenvalues higher than one, which explain 82.41% of the variance in original data.

The loadings of experimental variables on the first three rotated principal components (varifactors) may be found in (Table S3 Supplementary material). The first varifactor (VF1) groups variables with maximum concentrations near the town of Seville ($N\text{-}NH_4^+$, $N\text{-}NO_2^-$, $N\text{-}NO_3^-$, Co and Mn), and Cu, of which negative value indicate its opposite contribution. VF2 is contributed by those variables that exhibit the highest concentration within the agriculture area, such as SS, $P\text{-}PO_4^{3-}$, and Ni (with positive loadings), and by pH and conductivity (with negative contributions). Pb is the only variable that contributes to VF3, indicating its particular behavior in the Guadalquivir River. To elucidate the relations of these VFs with the activities developed in the river a plot of loadings of variables and scores of sampling stations, corresponding to VF1 and VF2, was done and showed in Fig. 5. Sampling stations are arranged in an orderly way forming an anticlockwise gyre around the origin, from first station to the last one.

In Fig. 5, three different groups of stations can be observed. One group is formed by stations located in the most populated urban zone (G1–G8), and a subgroup corresponding to the town of Seville (G6–G7) may be distinguished. The variables associated to these stations are $N\text{-}NO_2^-$, $N\text{-}NH_4^+$, $N\text{-}NO_3^-$, Co, and Mn, indicating their urban origin.

The second group comprised the stations located in the intermediate zone (G9–G17), being linked with $P\text{-}PO_4^{3-}$, SS, and Ni, confirming their agricultural origin. Although, Ni and $N\text{-}NO_3^-$ were related with agriculture and urban

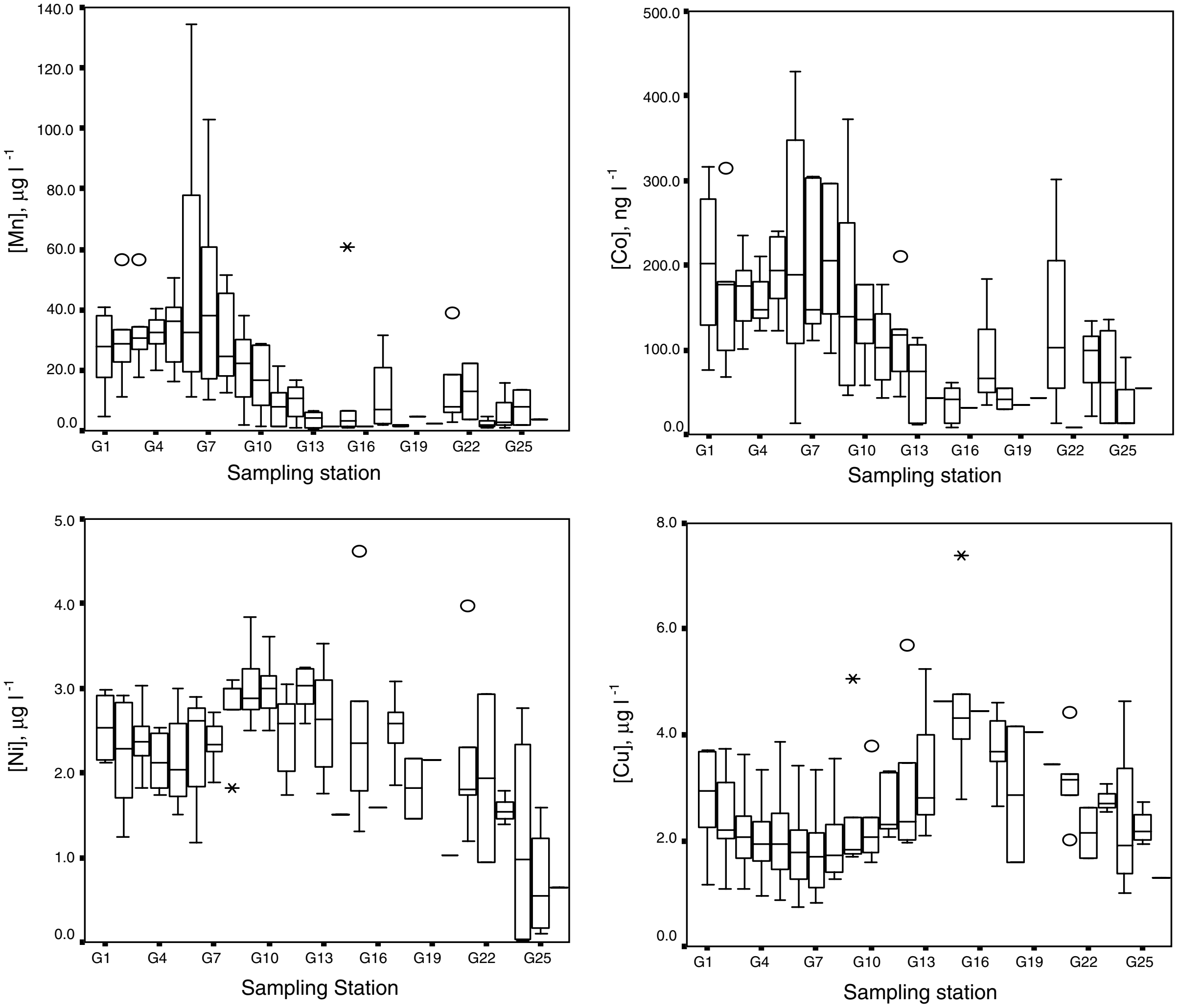

Fig. 3. Spatial variations of manganese, cobalt, nickel and copper in the sampling stations of Guadalquivir River. ○ and ✳ denote outliers with 1.5 × IQR and 3 × IQR, respectively.

zones, respectively, they were close to their border and probably present a shared origin.

The stations located in the estuary (G18–G26) were integrated in a third group, corresponding to saline waters. The variables associated with these stations were pH, Cd, and DO, and, of course, conductivity. Zn and specially Cu could not be clearly associated to a group, their origin being shared by agriculture activities and estuarine processes.

Finally, as expected, Pb presented a singular behavior without relation with any other variable.

3.5. Cluster analysis

Hierarchical cluster analysis (CA) was used to group both, sampling stations (based on water composition) and measured variables (based on spatial variations). Groups were formed using both Ward's and linkage between groups' (LBG) methods, and using Euclidean distance to quantify the similarity between objects. The classification patterns obtained by the two methods were very similar, so we just show the dendograms obtained with the LBG method for stations (Fig. 6) and variables (Figure S3, Supplementary material), respectively.

Fig. 6 shows a first division in two large clusters, one including freshwater stations and another with estuarine stations. Both clusters were subdivided in two new clusters. The first couple (freshwater) was formed, on the one hand, by stations of the urban zone (G1–G7), where independent behavior may be observed again for G6 and G7, and on the other hand by the stations affected by agriculture (G9–G12). In the second main cluster the stations are divided in those with low salinity (G13–G19) and high salinity (G20–G26).

So, in agreement with the results obtained for PCA, CA confirmed that the sampling stations in Guadalquivir River can be divided in three groups, urban, agricultural and estuary stations, based on water composition and related to the land uses.

When variables were analyzed (Figure S3, Supplementary material) we obtained two main clusters containing

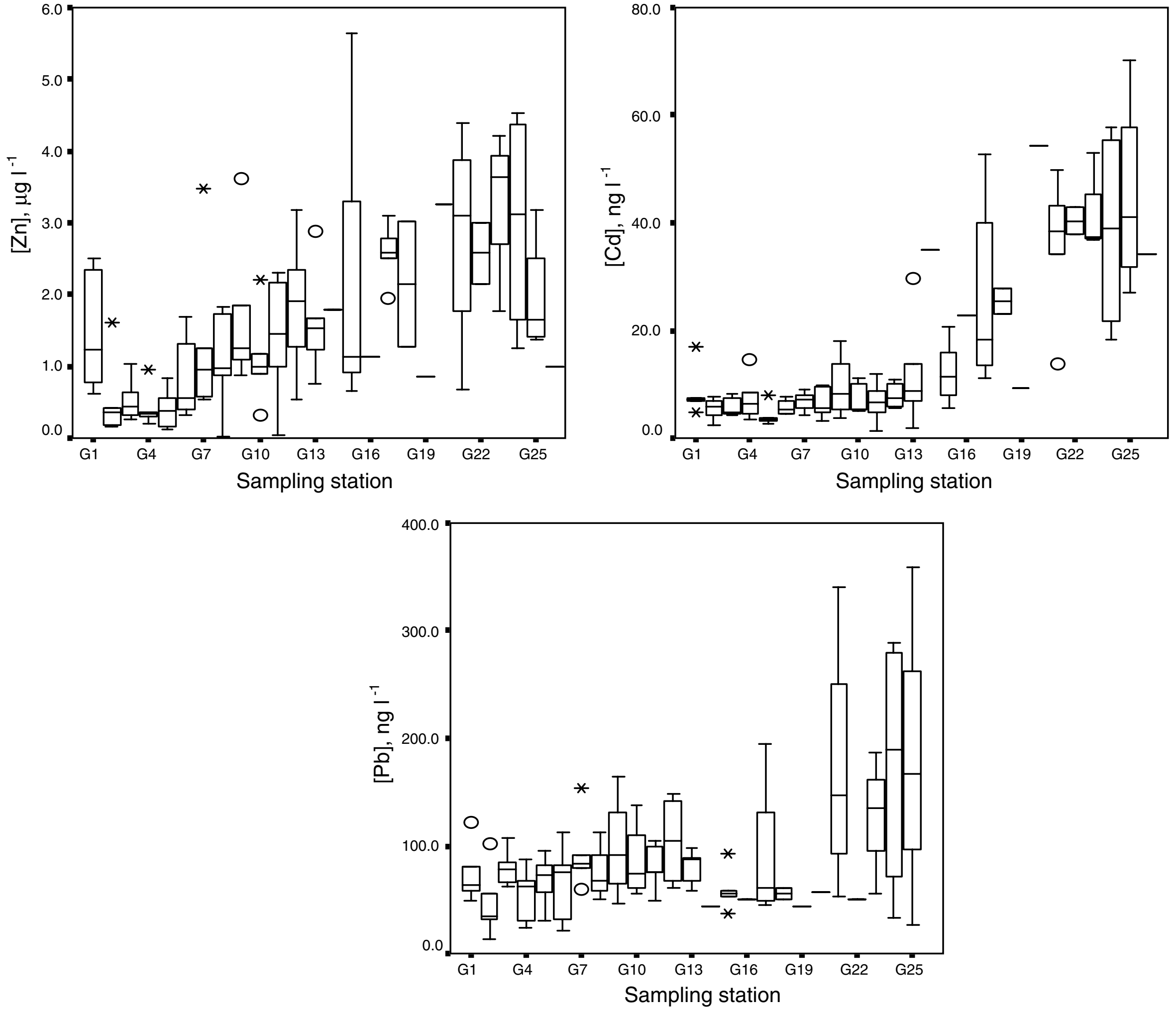

Fig. 4. Spatial variations of zinc, cadmium and lead in the sampling stations of Guadalquivir River. ○ and ∗ denote outliers with 1.5 × IQR and 3 × IQR, respectively.

Table 1
Mean values of dissolved trace element concentrations in the Guadalquivir river and in selected European rivers

Metal	River							
	Guadalquivir[a]	Guadalquivir[b]	Ebro[c]	Seine[d]	Marne[d]	Thame[e]	Vistula[f]	Eygoutier[g]
Mn ($\mu g\ l^{-1}$)	<1.00–134.65	20.65	–	6.26	3.92	10–12	5.3–583.8	–
Cu ($\mu g\ l^{-1}$)	0.74–7.40	2.64	1.75	2.23	1.80	4	0.9–90.0	1–24
Zn ($\mu g\ l^{-1}$)	<0.15–7.28	1.58	86.72	–	–	13–15	16.2–168.7	10–1400
Ni ($\mu g\ l^{-1}$)	<0.02–4.63	2.31	–	–	–	4–6	–	–
Co ($ng\ l^{-1}$)	7.98–790.62	147.21	–	–	–	–	250–3030	–
Cd ($ng\ l^{-1}$)	1.36–70.23	14.82	240	31	24	0–1000	510–730	–
Pb ($ng\ l^{-1}$)	13.13–3289.39	178.23	460	353.6	208	–	240–390	500–40000

[a] This study. Concentration ranges.
[b] This study. Mean values.
[c] Schuhmacher et al. (1995).
[d] Elbaz-Poulichet et al. (2006).
[e] Neal et al. (2006).
[f] Guéguen and Dominik (2003).
[g] Nicolau et al. (2006).

four sub-clusters. First, grouped N-NH_4^+, Mn, N-NO_2^-, N-NO_3^-, and Co, associated to urban activities. A second group included P-PO_4^{3-}, SS, and Ni, variables previously related to agriculture activities by PCA. A third cluster

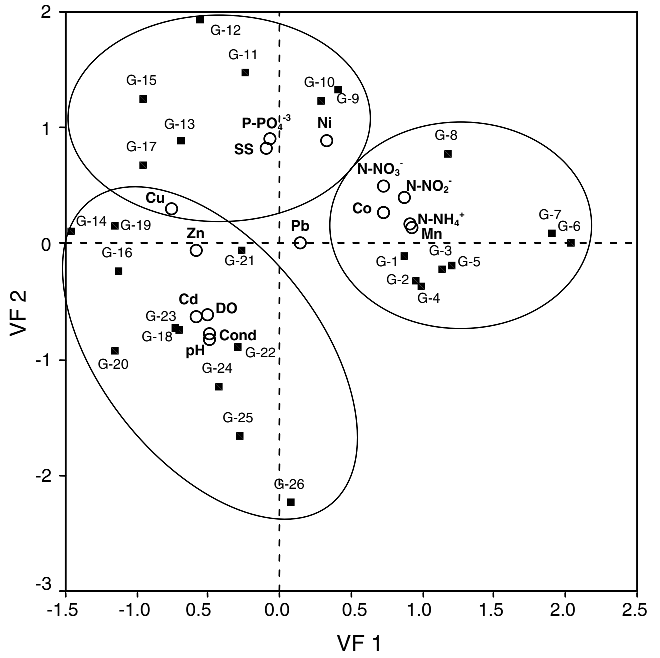

Fig. 5. Scores of sampling sites (■) and loadings of variables (○) on the plane defined by the first two rotated principal components.

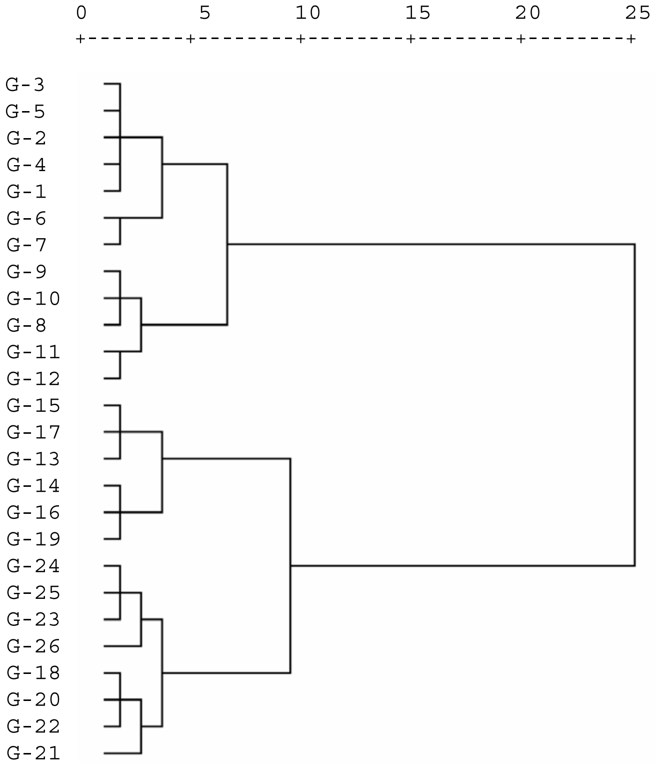

Fig. 6. Dendogram of the 26 sampling stations studied in the Guadalquivir River.

was formed by variables influenced by estuarine processes: pH, conductivity, Cd, DO, together with Zn. Finally, Cu and Pb formed independent clusters, confirming their particular behavior in Guadalquivir River.

4. Conclusions

The water quality of a river was established by analyzing dissolved heavy metals, as well as other parameters such as nutrients or physico-chemical variables. In the case of Guadalquivir River, we identified three different zones, with different water characteristics, mainly influenced by sewage, agriculture and estuarine processes, respectively. Besides, we identified the chemical variables that may be used to characterize each zone and the corresponding activities. Thus, water quality of urban zones was mainly controlled by N-NH$_4^+$, N-NO$_2^-$, Mn, and Co. Agriculture was linked to SS, P-PO$_4^{3-}$, and Ni, while Cd, pH, and conductivity were the variables related to estuarine zones.

If compared with our previous work (Mendiguchía et al., 2004), on the one hand, we have confirmed the preliminary conclusions about the three zones in the river. In addition, the inclusion of new variables has allowed a finer separation of these zones, especially of the intermediate one, and the estuarine zone, where two sub-zones could be separated. Besides, we have related some trace metals with specific zones or activities, e.g. Ni with agriculture, Cd with the estuary or Co with the urban-industrial zone.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2007.05.082.

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