

Fractionation and Distribution of Metals in Guadiamar River Sediments (SW Spain)

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Abstract Traditionally, the Guadiamar River (Seville, Southwest Spain) has received pollution from two different sources, in its upper section, from a pyrite exploitation (Los Frailes mine) and, in its lower section, from untreated urban and industrial wastes and from intensive agricultural activities. In 1998, the accidental spillage of about 6 million m³ of acid water and sludge from mine tailings to Guadiamar River worsened the pollution of an already contaminated area. The main polluting agents of the spillage were heavy metals. The total concentration of a metal provides scarce information about the effects on environmental processes or about the toxicity of the sediment samples. A more sophisticated fractionation of the sediment samples based on a species distribution can help to understand the behaviour and fate of the metals. This article describes a distribution study of the metals Al, Cd, Cu, Fe, Mn, Pb and Zn by fractionation analysis of sediments from eleven sample sites alongside the Guadiamar Riverbed. The samples were collected in summer 2002, four years after the spillage and after the area had been cleaned. Sequential extraction analysis resulted in the definition of four fraction categories: exchangeable metal (the most available fraction), reducible metal (bound to hydrous oxides of Fe and Mn), oxidizable metal (bound to organic matter and

sulphides) and a residual fraction (bound to minerals). Significant increases in the available fraction of several potentially toxic metal ions like Cd, Mn and Zn were found. The distribution pattern was variable along the River. At the site closest to the mineworks, the soluble forms of Cd, Mn and Zn were significantly more abundant than those downstream. Cu and Pb were present in the reducible fraction while Fe was present associated in the residual fraction.

Keywords Metal fractionation · Sediment · Guadiamar river · Mine spillage

1 Introduction

The Guadiamar River Basin is located in the southwest of the Iberian Peninsula in an area affected by urban and agriculture sewage pollution and with tradition on intensive mining activities (Cabrera et al. 1984). Some of the pollution sources, in the lower reaches of the River, are urban wastewaters and wastes from olive oil mills that reach the Guadiamar River from the affluent streams Ardachón and Alcarayón (Arribas et al. 2002) which pollute Guadiamar River with large amounts of organic matter, suspended solids and reduced nitrogen species. On the other hand, pyritic wastes from mining activities arrive Guadiamar River from its main affluent, the Agrío River (Cabrera et al. 1987; González et al. 1990; Riba et al. 2006; Rico et al. 1987). This pollution source contained significant

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amounts of heavy metals (Cd, Cu, Mn, Pb, Zn, etc.) present as sulphides and provided a low pH media that makes metallic forms readily available and, therefore, easy to propagate throughout the River basin.

In April 1998, the spillage of 6 millions of m³ of mining wastes (acidic waters and piritic sludge) severely polluted Guadiamar River basin with heavy metals which caused serious damages to the local ecosystem (Cabrera et al. 2008). High levels were found for the following metals: Fe, Zn, Pb, Cd, Cu and Mn, among others.

In order to reduce the possible negative effects of this pollution event, the Regional Government started to clean the affected area and to apply clay conditioners to immobilise heavy metal to prevent their propagation throughout the River basin.

Studies of the heavy metal pollution in the area have involved determination of total metal levels. Although these data are very useful for an immediate actuation to prevent the spread of the pollutants, they do not provide enough information about their impact on the environment. There is a direct relationship between physico-chemical speciation of an element and its toxicity, biological activity, bioavailability, solubility and etc. (Allen and Hansen 1996; Álvarez et al. 2008; Deaver and Rodgers 1996; Li et al. 2009; Mota and Simões 1996; Santos et al. 2002; Solís et al. 2002).

Several authors have investigated the effect of the accidental spillage on soil and sediments (Aguilar et al. 2004; Cabrera et al. 2008; Clemente et al. 2005; Kraus and Wiegand 2006; Riba et al. 2005; Riba et al. 2006). The distribution of heavy metals in different phases and forms in sediment samples can be determined using single and sequential extraction procedures (Meguellati et al. 1983; Ure et al. 1993). The phases or forms are operationally defined by means of reagents and procedures used to isolate a specific element fraction. Sequential extraction procedures provide information about the different reactive binding strengths of the metals in the different solid phases and about their potential reactivities under different physico-chemical environmental conditions. By means of this extraction procedure the mobility of the metals in the environment can be evaluated.

In the present work, we study the distribution of different metal fractions in sediments of the Guadiamar River basin based on the application of a sequential extraction procedure (Ure et al. 1993). Four metal fractions were determined: exchangeable, reducible,

oxidizable, and total residual metal. Exchangeable fraction corresponds to the metal fraction associated to water and acid-soluble species; reducible fraction corresponds to the metal fraction associated to iron and manganese oxides; oxidizable fraction corresponds to the metal fraction associated to organic matter; and total residual metal fraction corresponds to the metal fraction strongly associated to mineral matter being the more mobile forms exchangeable, reducible, oxidizable and total residual metal, in this order. This study completes a previous study carried out on the speciation of heavy metals in surface water from the same sampling sites in Guadiamar River (Alonso et al. 2004). Moreover, statistical analysis of the data by multiparametric methods is carried out to discover correlations which are not easily predicable and which are essential to establish indicators of metal pollution impact in a given geographical setting (eg. available/not available, recent/ancestral pollution).

2 Material and Methods

2.1 Sediment Sampling

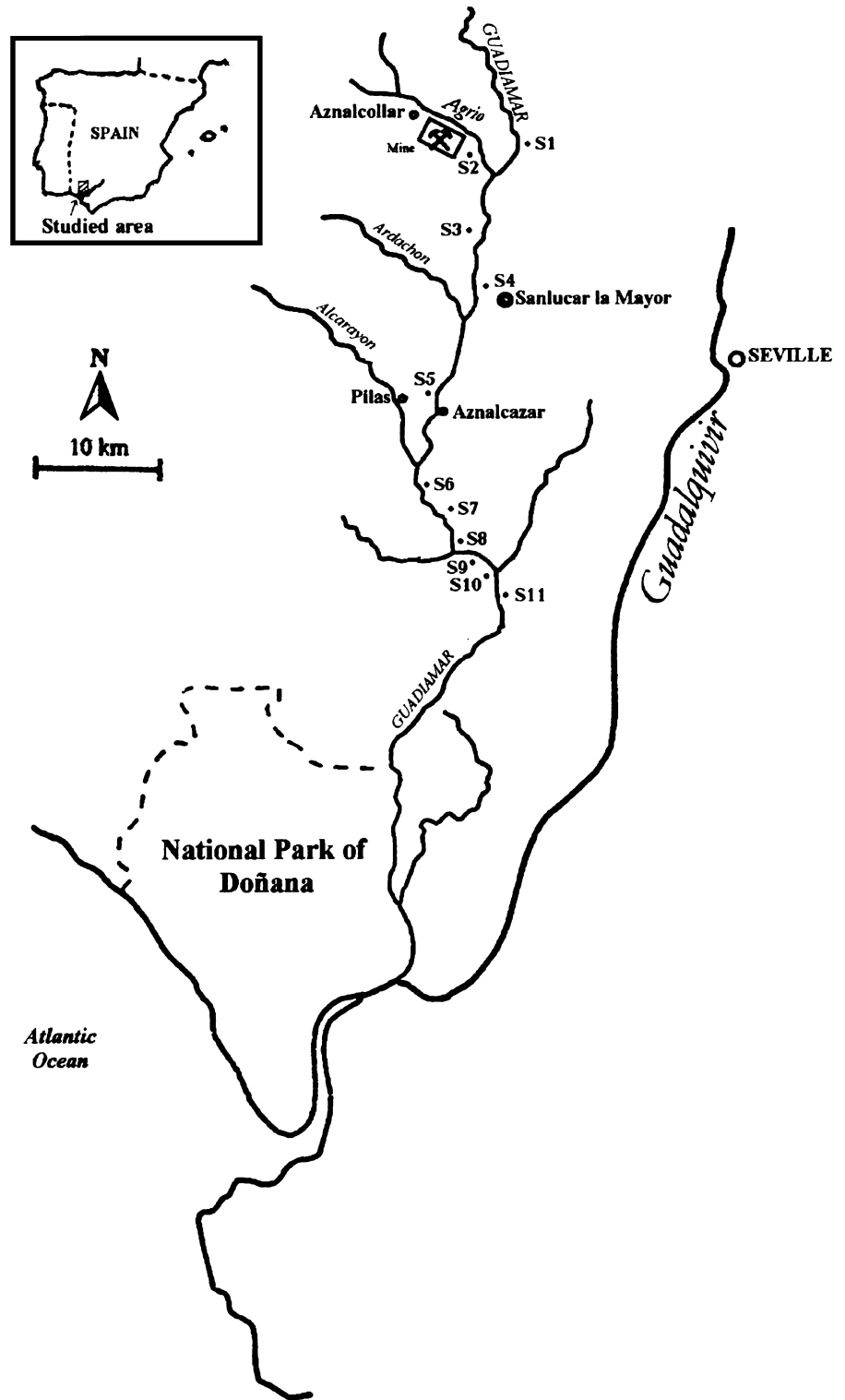
Sediment samples were collected in the summer of 2002, four years after the mining spillage occurred. Locations of sampling sites, named S1 to S11, are shown in Fig. 1. Sampling site 1 is located on the Guadiamar River, upstream of the mining influence. Sampling site 2 is located on Agrio River, downstream the piritic deposits. Sites 3 and 4 are situated below the confluence of Agrio River with Guadiamar River. Sites 5–11 are situated below the confluence of Ardachón and Alcarayón streams with Guadiamar River. These sites are the most affected by the effluents from olive-oil mills and urban wastewaters untreated.

The samples were collected according to previous reported methods (Fuchs et al. 1997; Leoni and Sartori 1997), stored in 1 L polyethylene containers, pre-cleaned with 10% nitric acid (v/v) solution, and maintained frozen at –30 C until analysis.

2.2 Sediment Analysis

Three replicates of each dried sample, sieved to particle size lower than 63 µm, were analysed for several known chemical variables related to the intake of heavy metals by the sediment such as loss at 500 C (mineral and

Fig. 1 Location of the eleven sampling sites



organic matter), pH and conductivity. These parameters were measured by the standard methods compiled by APHA (1998).

2.3 Heavy Metal Determination and Speciation

Al, Cd, Cu, Fe, Mn, Pb and Zn fractions were determined in a inductively coupled plasma atomic emission spectrometer (Fisons Instruments, Model 3410) after the sequential extraction procedure described by the BCR (now the Standards, Measurements and Testing Programme) from the European Commission (Ure et al. 1993). Direct calibration was used. Four metal fractions were determined: exchangeable, reducible, oxidizable and total residual metal.

2.3.1 Exchangeable Metal Ion

40 mL of a 0.11 mol/L acetic acid solution was added to 1 g of dry sediment sample contained in a 100 mL polypropylene centrifuge tube and previously sieved to particle size lower than 63 μm . The tube was then shaken at 40 rpm for 16 h at room temperature (approx. 20 C) in an end-over-end mechanical shaker (Agitaser, Barcelona, Spain). The extract was separated from the solid residue by centrifugation at 4000 rpm (Sigma 3-11 centrifuge). The liquid phase was transferred into a clean polyethylene container and stored at 4 C until analysis. The residue was washed with 20 mL of distilled water by shaking for 15 min and centrifugation.

2.3.2 Reducible Metal

40 mL of a hydroxylammonium chloride solution (0.1 mol/L, pH adjusted to 2 with nitric acid) was added to the residue obtained from section 2.3.1. and the extraction procedure at room temperature (approx. 20 C) described above was applied.

2.3.3 Oxidizable Metal

10 mL of an 8.8 mol/L hydrogen peroxide solution was carefully added, in small aliquots, to the residue obtained from section 2.3.2. The centrifuge tube was then covered with a watch glass and digested at room temperature for one hour with occasional manual shaking. Digestion was continued by heating the tube at 85 C in a water bath for one hour. The watch glass

was then removed and heating was maintained until the volume was reduced to 1–2 mL. Another 10 mL of hydrogen peroxide solution was added and the tube was again covered and heated at 85 C for one hour. Then, the cover was removed to reduce the volume to 1–2 mL as described above. 50 mL of an ammonium acetate solution (1 mol/L, adjusted to pH 2 with nitric acid) was added to the cool residue. The sample was then shaken, centrifuged and the extract was separated as described in section 2.3.1.

2.3.4 Total Residual Metal

A mixture of 10 mL of HF (40% w/w), 15 mL of HNO_3 (65% w/w) and 1 mL of HClO_4 (60% w/w) was added to the residue from step 3. After this, the digestion vessel was placed in the chamber of the Ethos 900 microwave apparatus (Milestone, Sorisole, Italy). Microwave extraction conditions, extraction time and power applied to sample treatment were those previously optimised and reported (Alonso et al. 2000). The results suggested that the conditions for achieving maximum recoveries were obtained at a power of 60% for 25 minutes. After digestion, the sample solution was allowed to air cool and then 4.00 g of boric acid was added. The solution was filtered through a 0.45 μm filter and quantitatively transferred to a 50 mL volumetric flask. It was diluted to volume with de-ionised water.

Total metal concentration was determined by calculating the sum of the concentrations of each of the metal species.

3 Results and Discussion

3.1 Physicochemical Parameters and Total Metal Concentration

Tables 1 and 2 show some physicochemical parameters and total Al, Cd, Cu, Fe, Mn, Pb and Zn, contents of the sediments and surface water from Guadiamar River. Surface water data were those reported previously by Alonso et al. (2004). The lowest pH values were measured in the sites closest to the mine, as occurred in the case of surface waters, due to the mining contamination in the area. On the other hand, downstream, after sampling site S5, the highest organic matter contents and conductivity values were obtained

Table 1 Comparison of physicochemical parameters of sediments (mean \pm SD, $n=5$) and surface water from Guadiamar River

| Sampling site | pH | | Conductivity ($\mu\text{S}/\text{cm}$) | | Organic matter (%) | Chemical oxygen demand (mg/L) |
|---------------|---------------|----------------------------|--|----------------------------|--------------------|-------------------------------|
| | Sediment | Surface water ¹ | Sediment | Surface water ¹ | Sediment | Surface water ¹ |
| S1 | 7.4 \pm 0.1 | 7.8 | 1365 \pm 184 | 336 | 2.6 \pm 0.9 | 41 |
| S2 | 6.9 \pm 0.2 | 7.8 | 1826 \pm 221 | 218 | 3.1 \pm 0.7 | 35 |
| S3 | 7.3 \pm 0.2 | 7.1 | 2152 \pm 324 | 1053 | 3.2 \pm 0.6 | 37 |
| S4 | 7.4 \pm 0.1 | 7.5 | 2231 \pm 316 | 1021 | 3.4 \pm 0.9 | 38 |
| S5 | 7.3 \pm 0.2 | 7.5 | 2361 \pm 314 | 944 | 4.1 \pm 1.1 | 67 |
| S6 | 7.2 \pm 0.1 | 7.8 | 2241 \pm 296 | 1228 | 12.3 \pm 1.5 | 76 |
| S7 | 7.8 \pm 0.1 | 7.8 | 2664 \pm 345 | 1058 | 18.5 \pm 1.3 | 58 |
| S8 | 7.9 \pm 0.1 | 8.0 | 2687 \pm 398 | 1126 | 17.1 \pm 1.8 | 62 |
| S9 | 7.8 \pm 0.3 | 7.7 | 2789 \pm 325 | 1630 | 19.3 \pm 1.3 | 68 |
| S10 | 8.0 \pm 0.3 | 7.6 | 2856 \pm 345 | 1245 | 20.4 \pm 1.5 | 68 |
| S11 | 8.1 \pm 0.2 | 7.8 | 2923 \pm 356 | 1996 | 21.5 \pm 1.7 | 91 |

¹ Values from Alonso et al. (2004)

due to the contamination by dumping of untreated wastes that affect downstream waters of Guadiamar River. Patterns of heavy metals characteristic of mining spills: Cd, Mn and Zn (Fig. 2), observed over the sampling network were very similar to those obtained in surface waters. The highest concentrations of these metals were found nearest to the mine and tended to decrease in the sites further downstream (Alonso et al. 2004). The metals Cu and Pb, as occurred in surface waters, were found at lower concentration levels than other metals from the spillage (Fig. 2). These metals presented different evolutionary trends in sediments compared to trends in surface waters; they were present at the highest levels in sediments nearest to the mine and tended to decrease downstream. Finally, Al and Fe presented similar and parallel trends to those observed in surface waters with a general tendency to increase in concentration downstream (Fig. 2). In the case of Fe, this fact was due to its mobilisation from soils where clay soil conditioners had been applied; and in the case of Al, the marked increase after sampling site S5 was due to wastewater dumping.

3.2 Metal Fractionation

Figure 3 shows the percentage of metal distribution in chemical fractions in sediments from Guadiamar River. The most characteristic metals, Cu, Cd, Pb and Zn, presented a similar distribution of metal

species to that obtained on surface waters (Table 2). The highest percentages of available species of Cd and Zn were recorded in the sites nearest the mining spillage and then they tended to decrease downstream whereas an increase of the less mobile species, in this case oxidizable and residual species, occurs.

Similarly, Cu and Pb were present in higher percentages in the less available forms, as occurred in surface waters and were associated, for example as reducible forms, to Fe and Mn. The most available forms of Mn were found nearest the mining spill and then they decreased further downstream as in the case of Cd and Zn. Finally, Al and Fe were present in all sampling sites in the less mobile forms. Fe was mainly associated to the primary sediment fraction and Al presented a clear distinction between two sampling areas (sampling sites from S1 to S5 and from S6 to S11). In the sampling area from S1 to S5, Al was present, in a low concentration level, associated to the mineral fraction of the sediment. Then, after sampling site S5, Al was present in oxidizable forms what reflects its association to organic matter and, hence, its origin from wastewater sources.

In Fig. 4, a comparative between the distribution of metallic species in sediment samples and in surface water is shown. The distribution of metallic species in surface water was obtained from Alonso et al. (2004). The comparative was made from the sum of the

Table 2 Comparison of metal content of sediments (mean \pm SD, $n=5$) and surface water from Guadamar River

| Sampling site | Zn | | Cd | | Pb | | Cu | | Mn | | Fe | | Al | |
|---------------|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Sediment ($\mu\text{g}/\text{kg}$) | Surface water ¹ ($\mu\text{g}/\text{L}$) | Sediment ($\mu\text{g}/\text{kg}$) | Surface water ¹ ($\mu\text{g}/\text{L}$) | Sediment ($\mu\text{g}/\text{kg}$) | Surface water ¹ ($\mu\text{g}/\text{L}$) | Sediment ($\mu\text{g}/\text{kg}$) | Surface water ¹ ($\mu\text{g}/\text{L}$) | Sediment ($\mu\text{g}/\text{kg}$) | Surface water ¹ ($\mu\text{g}/\text{L}$) | Sediment ($\mu\text{g}/\text{kg}$) | Surface water ¹ ($\mu\text{g}/\text{L}$) | Sediment ($\mu\text{g}/\text{kg}$) | Surface water ¹ ($\mu\text{g}/\text{L}$) |
| S1 | 66.5 \pm 16.5 | 86.7 | 2.2 \pm 0.1 | 14.6 | 5.8 \pm 4.0 | 98.7 | 17.0 \pm 6.5 | 14.4 | 277 \pm 157 | 53.4 | 27568 \pm 3006 | 739.3 | 126 \pm 102 | 785.0 |
| S2 | 4955 \pm 3010 | 138.5 | 15.3 \pm 8.4 | 3.3 | 119 \pm 68 | 20.0 | 392 \pm 198 | 13.0 | 1438 \pm 1008 | 19.7 | 49940 \pm 6082 | 425.4 | 231 \pm 209 | 398.8 |
| S3 | 651 \pm 285 | 1000.8 | 5.5 \pm 1.7 | 286.0 | 26.7 \pm 17.0 | 13.1 | 127 \pm 44 | 30.9 | 799 \pm 476 | 1029.5 | 40306 \pm 2888 | 1051.0 | 1068 \pm 1026 | 1284.1 |
| S4 | 2580 \pm 1942 | 758.5 | 11.8 \pm 7.6 | 257.3 | 109 \pm 100 | 18.8 | 209 \pm 138 | 23.1 | 1925 \pm 1508 | 922.9 | 7372 \pm 3393 | 977.2 | 739 \pm 717 | 1157.0 |
| S5 | 1162 \pm 597 | 306.6 | 3.3 \pm 2.1 | 110.0 | 72.1 \pm 61.8 | 24.5 | 328 \pm 230 | 23.4 | 605 \pm 273 | 391.1 | 33032 \pm 1137 | 1850.6 | 1437 \pm 1408 | 1713.9 |
| S6 | 1810 \pm 1066 | 223.7 | 12.8 \pm 7.3 | 86.3 | 95.0 \pm 61.2 | 17.5 | 319 \pm 179 | 37.3 | 714 \pm 380 | 338.8 | 35715 \pm 4717 | 2145.4 | 12673 \pm 9798 | 2388.6 |
| S7 | 1441 \pm 725 | 465.2 | 9.7 \pm 4.6 | 58.1 | 66.7 \pm 45 | 49.1 | 290 \pm 174 | 39.7 | 921 \pm 527 | 617.9 | 38572 \pm 3881 | 2694.7 | 13216 \pm 10852 | 3243.6 |
| S8 | 1102 \pm 513 | 185.4 | 6.9 \pm 3.0 | 45.4 | 48.2 \pm 32.6 | 35.5 | 199 \pm 100 | 30.5 | 871 \pm 487 | 318.6 | 44608 \pm 2873 | 2725.5 | 14647 \pm 12941 | 2593.7 |
| S9 | 763 \pm 308 | 187.4 | 4.2 \pm 1.5 | 53.3 | 29.7 \pm 20.2 | 77.1 | 107 \pm 25 | 25.2 | 820 \pm 452 | 351.3 | 50643 \pm 1902 | 2697.5 | 16078 \pm 14216 | 3600.0 |
| S10 | 832 \pm 384 | 241.7 | 4.0 \pm 1.3 | <LOD ² | 35.5 \pm 25.3 | 30.6 | 89.5 \pm 30.1 | 37.6 | 824 \pm 446 | 452.4 | 41492 \pm 1412 | 3271.5 | 14676 \pm 13264 | 4461.6 |
| S11 | 901 \pm 516 | 255.6 | 3.9 \pm 1.2 | 1.1 | 41.3 \pm 30.3 | 54.5 | 72.1 \pm 34.8 | 39.9 | 828 \pm 442 | 690.5 | 32340 \pm 956 | 4270.3 | 13274 \pm 11748 | 6907.5 |

¹ Values from Alonso et al. (2004)² <LOD: below limit of detection

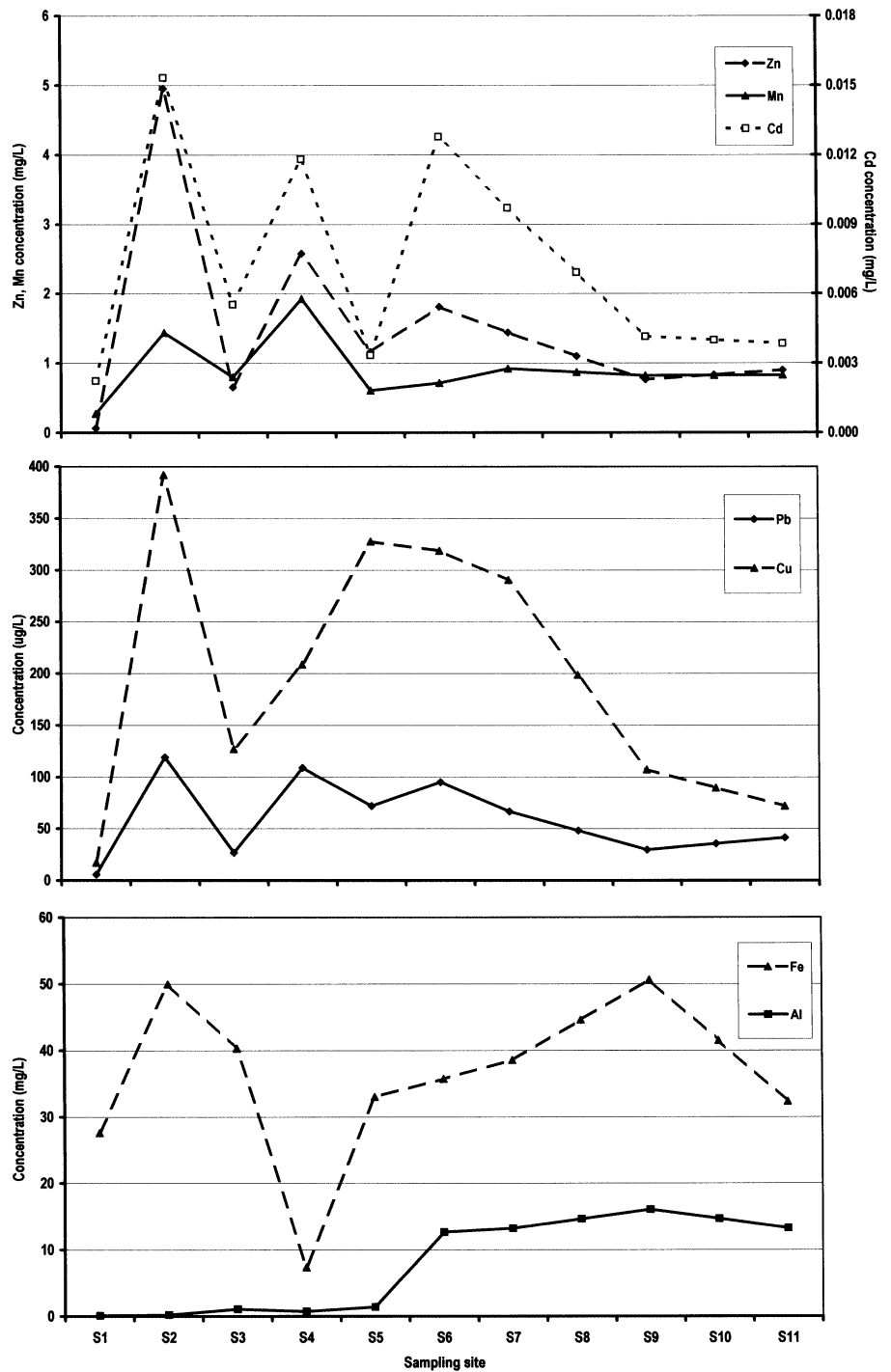
concentrations of all analysed species differentiating two zones: zone I (from S1 to S4), affected by the discharge of Agrio River; and zone II (from S5 to S11), affected by the confluence of Ardachon and Alcarayón streams with Guadamar River. Metal fractions of surface waters were analogous (in mobility) to those of sediments: labile metal, H⁺ exchangeable metal ions, metal associated to dissolved organic matter and metal associated to suspended matter (Alonso et al. 2004). In general, a decrease of the concentration of the more mobile fractions is observed, with the consequent increase of the species less available. This fact is related to the change of the physicochemical characteristics of the system downstream (increase of the content in organic matter, reduction of pH, etc.), what conditions the speciation pattern.

3.3 Statistical Analysis: Correlation and Factor Analysis

Correlation analysis was applied to measure the relationship strength between variables; the closest to -1.0 or +1.0 the correlation coefficient between two variables is the strongest relationship exists. Correlation analysis among variables revealed good correlations between Al and organic matter, showing that this metal comes from a wastewater contamination of the river. Similarly, good correlations were found between Cd, Cu, Pb and Mn, Zn, what is characteristic of the mining contamination of the area. Finally, good correlations were also obtained between the same types of metal forms, derived from the use of a common extract for their determination.

Factor analysis, a statistical method used to explain variability among observed variables, was applied to elucidate the relevant contamination patterns. Variables evaluated were pH, conductivity, organic matter, total metal concentration and the concentration of each of the metals in each of the metal forms evaluated. Factor analysis showed the existence of two significant factors: a first factor, explaining 35% of the variance, that was comprised by Cd, Mn, Pb and Zn and the exchangeable and reducible forms of these metals among other parameters; and a second factor, explaining 18% of the variance, that was comprised by Cu and by the oxidizable forms of Cd, Cu, Fe and Zn. Taking into account the parametric composition of each factor, the first factor would reflect the pollution in the area affected by the mining spillage, and the second factor

Fig. 2 Variation of Zn, Mn, Cd, Pb, Cu, Fe and Al contents in the sampling sites



would explain the contamination due to previous mining activities because of the predominance of the less available metal forms. Representation of factor 1 versus factor 2 (Fig. 5), shows the existence of two different

groups of parameters: one comprised by the parameters that reflect a previous mining contamination and another group that reflect the contamination due to the most recent mining spillage.

Fig. 3 Percentage of metal fractions in sediment samples from Guadiamar River

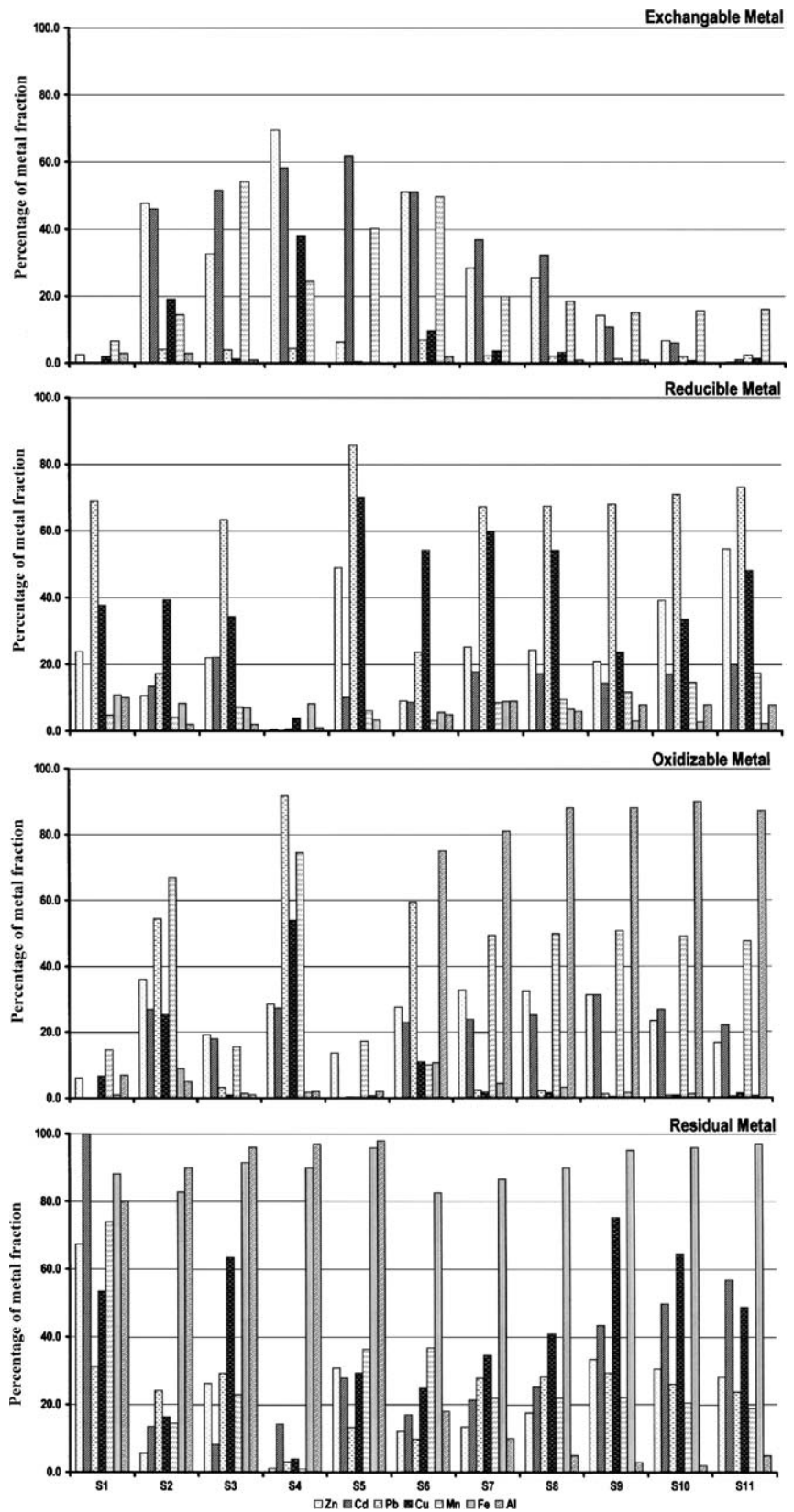
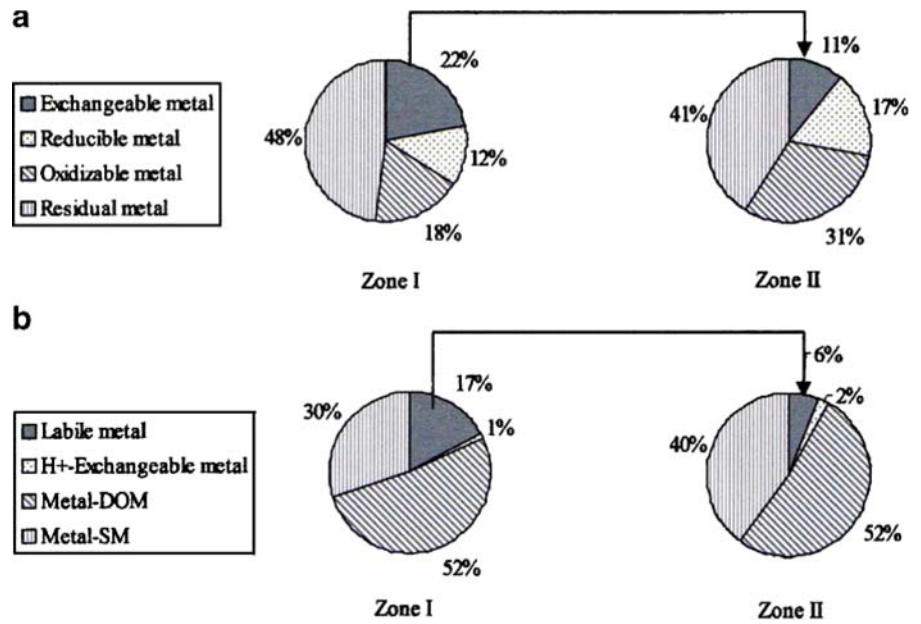


Fig. 4 Comparative between the distribution of metallic species in sediment (a) and surface water (b) samples from zone I (S1 to S4) and zone II (S5 to S11) (DOM=dissolved organic matter, SM=suspended matter). Percentage values in surface waters were obtained from Alonso et al. (2004)



4 Conclusions

There is a clear correlation between the evolving trends of the most significant parameters of sedi-

ments and surface waters in relation to common non-specific parameters as total metals and metal forms. This fact results in the existence of two clearly different areas on the basis of the different

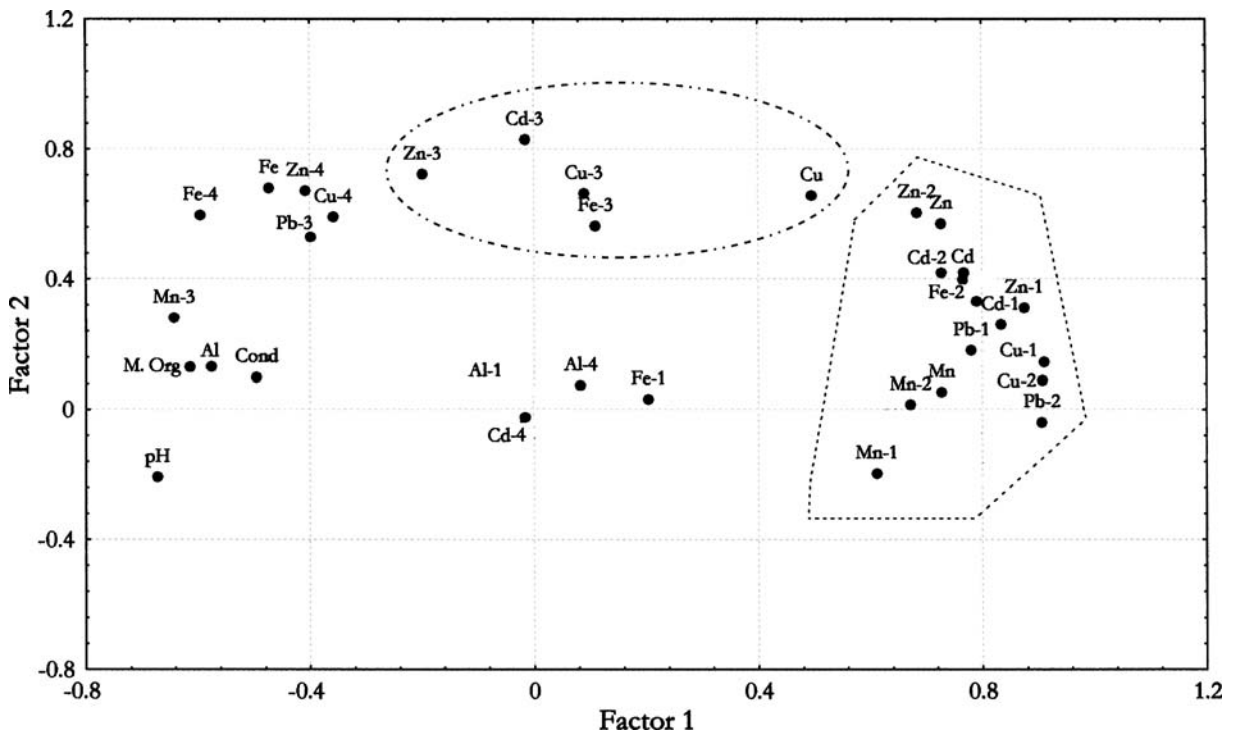


Fig. 5 Representation of Factor 1 versus Factor 2. Number at the right of the metal symbol indicates the metal form of the element (1: metal in exchangeable form; 2: metal in reducible form; 3: metal in oxidizable form; 4: total residual metal; without number: total metal)

pollution sources in each area and how these affect metal fractionation dynamics.

The fractionation trends observed in water and sediments samples were similar. According to this fact, the studied area can be divided into two separate zones. Water quality of Guadiamar River was severely affected by three of its main streams. One of the streams, Agrio River, provides water at a low pH containing labile forms of heavy metals present as sulphides and pyritic wastes. Because all of that, a first zone between sampling sites S1 and S4 (Zone I) can be differentiated. Downstream, discharges of Ardachón and Alcarayón streams, spill urban wastewaters and agricultural food wastes to Guadiamar River allows to differentiate a second zone between sampling sites S5 and S11 (Zone II). The metal distribution obtained in the samples confirms the above mentioned spatial differentiation. Indeed, the highest percentages of available forms were observed in Zone I, while in Zone II (downstream reach) higher amounts of the less available forms were measured.

The statistical treatment of the data by means of correlation and factor analysis allowed checking the obtained conclusions. Good correlations were obtained between parameters with similar origin. For example, correlations were found between characteristic metals of mining contamination, not only regarding to their total concentration but also regarding to the concentration of the metallic species. The factor analysis allowed to establish two sources of mining contamination, an ancestral source that was represented by the less mobile metallic forms and a recent source represented by the available forms that comes from the mining spillage.

The study of heavy metal fractionation in different samples from Guadiamar River, has demonstrated to be an excellent tool to know not only about the mobility degree of the polluting agents but also about their possible evolution.

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