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TECHNICAL ARTICLE

# Statistical Contrast Analysis of Hydrochemical Parameters Upstream of the Tidal Influence in Two AMD-Affected Rivers

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**Abstract** The Iberian Pyrite Belt (IPB), SW Spain, has been exploited since ancient times, and previous studies have compared different parameters in the Tinto and Odiel Rivers, the principal rivers that cross the IPB. We used classical statistics to draw contrasts between the two rivers. Samples were collected at two sites, one in the Tinto River, and the other in the Odiel, immediately upstream of tidal influence. Both rivers are strongly contaminated by acid mine drainage (AMD). However, the results suggest a distinctive, although somewhat parallel, geochemical behavior. The pattern of affinity between parameters differs because in addition to AMD, the Odiel River receives important contributions from non-contaminated catchments, while the Tinto River is the main receptor of drainage from the Rio Tinto mine. The applied statistical approach revealed that pH and electrical conductivity present a similar temporal evolution, which point to an identical geochemical signature; this indicates that both systems are similarly affected by contamination from the same pyritic area.

**Keywords** Iberian Pyrite Belt · Metals · Pollution · Odiel River · Tinto River

## Introduction

Acid mine drainage (AMD) can introduce high concentrations of iron, copper, zinc, aluminum, sulfuric acid, and metalloids, such as arsenic, into the aquatic environment. The low pH and acidity promote contaminant dissolution and increase the metallic load of these waters. These characteristics can drastically affect water quality and ecology (Nordstrom et al. 1999). Damage to ecosystems can range from sublethal effects, in cases of low contaminant levels enhanced by bioaccumulation and biomagnification, to severe modifications that cause the disappearance of riverine biodiversity and make the water resources useless for human, agricultural, or industrial use (Grande et al. 2010a). AMD can impose stress conditions to most living organisms, and can lead to the development of an extreme environment dominated by acidophilic and acid tolerant organisms (Valente and Gomes 2007). The effects tend be more serious if AMD affects transition environments (estuaries) and coastal systems, such as occurs in the Tinto and Odiel rivers.

AMD results from the oxidation of sulfides, especially iron sulfides such as pyrite ($FeS_2$). The process may be strictly inorganic or may be catalyzed by chemoautotrophic microorganisms. The low pH favors colonization by acidophilic bacteria and archaebacteria, which increases the oxidation rate of sulfide minerals (Cánovas et al. 2007). In addition, there is a complex chain of biotic and abiotic secondary reactions involving other minerals (Förstner and Wittmann 1983). These mineral–water interactions result in a set of soluble contaminants that are mobilized by superficial water or by runoff, leading to an acidic, metal-, and sulfate-rich solution that contaminates receiving watersheds. Although pyrite oxidation is inherently a natural phenomenon, the rhythms and conditions of production allow differentiation between the natural geochemical process and mining-induced AMD (EMCBC 1996).

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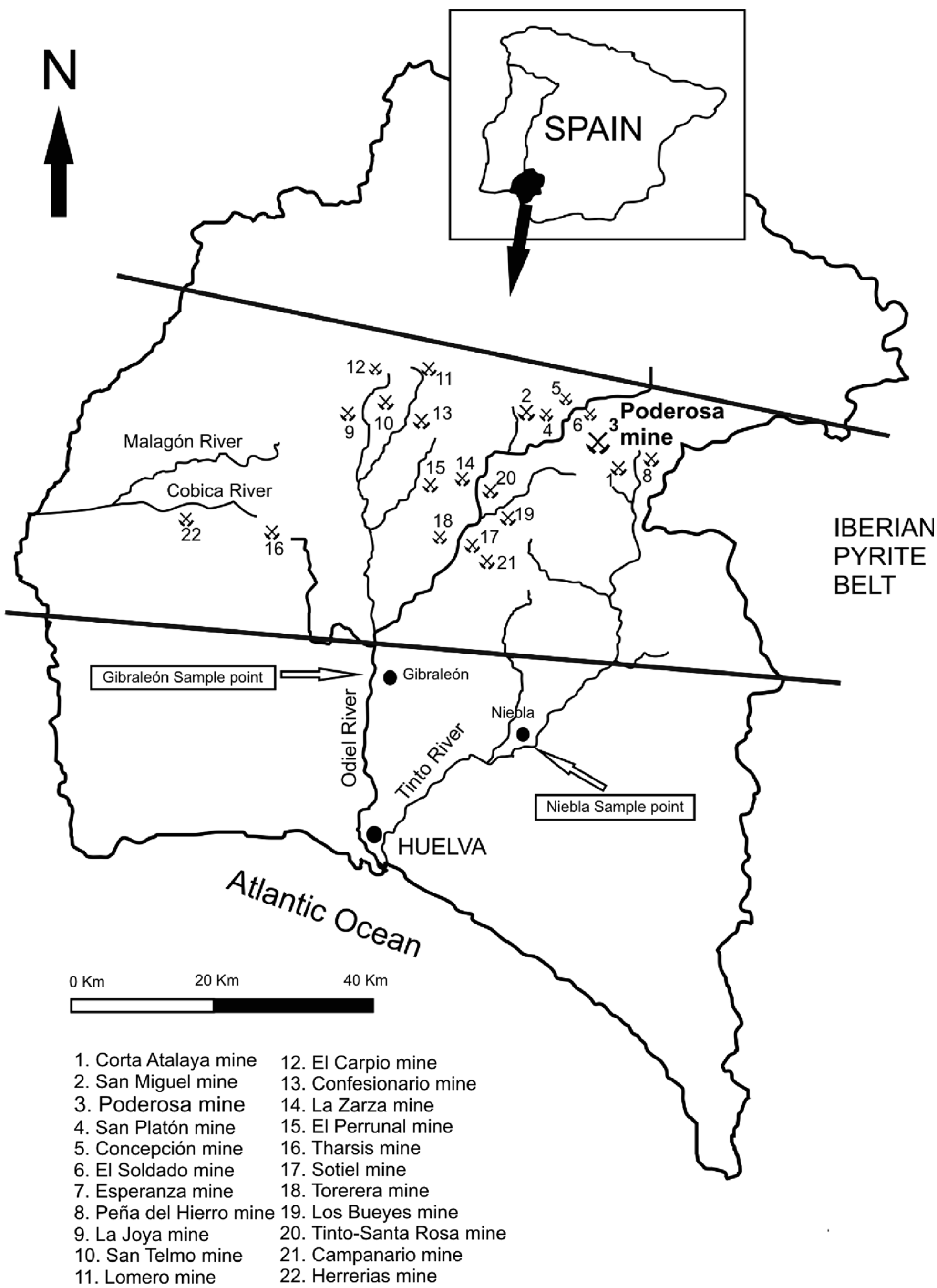
## Study Area

The Iberian Pyrite Belt (IPB) (Fig. 1) in SW Spain is about 230 km long and 30 km wide. It extends from Seville in southern Spain to the western coast of Portugal, crossing the Huelva province. This province is known for its metallogenic relevance, as it contains numerous giant and supergiant massive sulfide ore deposits (Sáez et al. 1999). This has made the IPB one of the most important mining regions in the world. The first mining dates back to the Copper Age (Nocete and Linares 1999), which was characterized by the production of copper from carbonates (azurite and malachite), oxides (cuprite and tenorite), and even sulfides, such as chalcosite and covelite (Nocete et al. 2005; Sáez et al. 2003). As a result, the region has numerous abandoned and active mining works that provide an inexhaustible source of acidity, sulfates, and metals (Azcue 1994).

The study area has a semi-arid Mediterranean climate, with an annual precipitation of about 630 mm year$^{-1}$, mild temperatures (averaging 17.1 °C) and a temperature range of 49 °C. Rainfall occurs mainly in the autumn and winter

**Fig. 1** Location map



seasons, with drought conditions in the summer and part of the spring (Jimenez 2009).

The AMD processes that affect the regional drainage network have been broadly described (Aroba et al. 2007; Borrego 1992; Borrego et al. 2002, 2011; Braungardt et al. 1998; Carro et al. 2011; Davis et al. 2000; de la Torre et al. 2009, 2010, 2011; Elbaz-Poulichet et al. 1999, 2000, 2001; Grande 2011; Grande et al. 2000, 2003a, b, 2005a, b, 2010a, b, c, d, e, 2011a, b; Jiménez et al. 2009; Leblanc et al. 2000; Sáinz et al. 2002, 2003a, b, 2004, 2005). The Tinto and Odiel rivers (Fig. 1) are paradigmatic examples of this type of contamination.

The geological nature of the Pyrite Belt, with its massive sulfides, causes one of the biggest AMD-related pollution problems worldwide. The strong acidity and high concentration of metals in water and sediments has resulted in the loss of the aquatic flora and fauna, with the exception of some microorganisms well-adapted to extreme environments (Sanchez-España et al. 2005). The Odiel River clearly demonstrates the result of AMD processes in the SW Iberian Peninsula (Grande et al. 2000; Sáinz et al. 2002). It starts in the mountains of Aracena (Huelva, Spain) and its water has an excellent general quality index for 24 km. AMD pollution begins when the river passes near Concepción Mine, and continues down to the river mouth. The Tinto River, whose hydrographic development coincides with that of the Odiel, carries contamination received from the exploitation of Rio Tinto Mines for its entire length.

Several authors have conducted studies that compared different parameters in both rivers. For example, Elbaz-Poulichet et al. (1999) focused their attention on the concentration of dissolved and particulate rare-earth elements. Olías et al. (2006) estimated the dissolved contaminant load transported by both rivers and Nieto et al. (2007) described the dissolved contaminant load and analyzed its seasonal variation. The same authors presented results of toxicity and bioaccumulation tests performed with estuary sediments to measure the mobility of the toxic metals. Cánovas et al. (2007) established relationships among several parameters in both rivers by comparing their temporal evolution and by using principle component analysis; in addition, they also focused on the speciation of Fe. Egal et al. (2008) determined the isotopic composition of Fe and Fe-oxides and sulfides from the Tinto and Odiel basins. Sarmiento et al. (2009) studied the speciation of Fe and As in both rivers. Pérez-López et al. (2011) quantified the annual amount of metals discharged by industrial activity into the Huelva River estuary. Grande et al. (2011a) compared distinct parameters analyzed in the same samples that were used in the present work, using fuzzy logic approaches. In order to complete and deepen this comparative analysis, the present work focused applied classical statistics to data from samples obtained at two sites, one in the Tinto River, and the other in the Odiel, immediately upstream of tidal influence (Fig. 1). This was intended to highlight potential differences in the physical–chemical behavior of the two rivers, which in both cases receive substantial AMD input from the IPB.

## Materials and Methods

Samples were collected daily from mid-September 2007 to the end of May 2008. This coincides with the period in which the Tinto River carries contaminants, since in May, after rainfall has ceased, there is no water flow (Grande et al. 2011a). Two samples were taken at each point in 100 mL polyethylene bottles, adding nitric acid at 1 % concentration to one of them to keep the pH below 2 SU. The other sample was kept unacidified for subsequent sulfate analysis. The pH and electrical conductivity (EC) were measured in situ using a Crinson MM40 portable multimeter. Redox potential was measured with an Oakton Eutech (model Waterproof ORPTestr 10) pocket tester. The samples were refrigerated and taken to the laboratory for analysis. For each sample, pH, EC, and redox potential, as well as sulfates, As, Cd, Fe, Zn, and Mn were determined.

All samples underwent preliminary filtering using Sartorius 11406-47-ACN 0.45 µm cellulose nitrate filters. All the reagents used were of analytical grade or higher, from Merck or Panreac. Ultra-pure water produced with a Milli-Q water purification system was used. Dissolved sulfates were measured using a Machery-Nagel PF-11 photometer. Fe, Cu, Mn, and Zn were analyzed by atomic absorption (AA) using a Perkin Elmer AAnalyst 800 atomic spectrometer and certified patterns. Cadmium (Cd) was analyzed by electrothermal AA spectrometry, using an AAnalyst 800 graphite furnace, equipped with a Zeeman background corrector and an electron discharge lamp. Arsenic (As) was determined using Perkin Elmer Fias 100 flow-injection equipment.

## Results

### Statistical Summary

Tables 1 and 2 show the statistical summary for the parameters analyzed in the Odiel and Tinto Rivers, respectively. The Odiel River has higher average pH values (3.35 compared with 2.62 in the Tinto River). The minimum pH values were 1.32 and 2.07 in the Tinto and Odiel, respectively. Similarly, the maximum pH was 3.4 in the Tinto River and 4.36 in the Odiel. On average, the Tinto

**Table 1** Statistical summary of variables obtained in the samples recollected in the Odiel River

| | Mean | Median | SD | Variance | Minimum | Maximum | Lower quartile | Upper quartile |
|---|---|---|---|---|---|---|---|---|
| pH O | 3.35 | 3.37 | 0.428779 | 0.183851 | 2.07 | 4.36 | 3.09 | 3.7 |
| Cond O (μS $cm^{-1}$) | 1,064.08 | 1,083 | 339.699 | 115,395 | 370.66 | 2,190 | 931 | 1,222 |
| Redox O (mV) | 497.61 | 513 | 71.4177 | 5,100.49 | 311.66 | 930 | 472.5 | 541 |
| As O (μg $L^{-1}$) | 0.3761 | 0.393 | 0.290938 | 0.0846448 | 0.054 | 2.029 | 0.252 | 0.65 |
| Cd O (μg $L^{-1}$) | 33.4594 | 34.65 | 16.7715 | 281.282 | 6.726 | 85.75 | 23.59 | 46.42 |
| Cu O (mg $L^{-1}$) | 3.79563 | 4.1 | 1.87176 | 3.5035 | 0.242 | 9.019 | 3.396 | 5.45 |
| Fe O (mg $L^{-1}$) | 6.1127 | 5.34 | 5.85869 | 34.3243 | 1.76 | 31.37 | 3.543 | 9.78 |
| Zn O (mg $L^{-1}$) | 9.20405 | 9.652 | 4.28989 | 18.4031 | 0.731 | 20.25 | 7.138 | 13.28 |
| Mn O (mg $L^{-1}$) | 7.22761 | 7.653 | 3.69699 | 13.6677 | 0.562 | 16.5 | 5.409 | 11.27 |
| $SO_4^{2-}$ O (mg $L^{-1}$) | 362.137 | 376 | 275.607 | 75,959.4 | 111 | 1,460 | 252 | 504 |

**Table 2** Statistical summary of variables obtained in the samples recollected in the Tinto River

| | Mean | Median | SD | Variance | Minimum | Maximum | Lower quartile | Upper quartile |
|---|---|---|---|---|---|---|---|---|
| pH T | 2.53875 | 2.62 | 0.370271 | 0.1371 | 1.315 | 3.4 | 2.365 | 2.86 |
| Cond T (μS $cm^{-1}$) | 2,239.75 | 2,367.5 | 809.919 | 655,969 | 757 | 5,493.33 | 1,918 | 2,722.5 |
| Redox T (mV) | 837.523 | 605.3 | 620.124 | 384,554 | 451.5 | 3,493 | 554.48 | 1,515 |
| As T (μg $L^{-1}$) | 41.6999 | 43.97 | 26.9319 | 725.329 | 4.838 | 141.4 | 31.87 | 70.65 |
| Cd T (μg $L^{-1}$) | 93.3868 | 99.11 | 43.4946 | 1,891.78 | 24.44 | 246.8 | 68.608 | 132.25 |
| Cu T (mg $L^{-1}$) | 23.8473 | 25.32 | 14.8881 | 221.657 | 3.895 | 74.13 | 19.4 | 30.71 |
| Fe T (mg $L^{-1}$) | 316.428 | 361.1 | 365.407 | 133,523 | 46.3 | 1,485 | 155.3 | 555.8 |
| Zn T (mg $L^{-1}$) | 20.2608 | 19.62 | 17.4693 | 305.177 | 3.42 | 77.51 | 14.02 | 30.54 |
| Mn T (mg $L^{-1}$) | 10.3656 | 9.99 | 6.4892 | 42.1098 | 3.756 | 32.37 | 7.784 | 12.675 |
| $SO_4^{2-}$ T (mg $L^{-1}$) | 370.541 | 396 | 150.259 | 22,577.8 | 123 | 776 | 288 | 494 |

River was more contaminated, with the exception of sulfates, which were similar: 376 mg $L^{-1}$ in the Odiel and 396 mg $L^{-1}$ in the Tinto).

Continuing this analysis regarding the parameters measured in situ, the results show that EC averaged 2,367.50 mS $cm^{-1}$ in the Tinto River and 1,083 mS $cm^{-1}$ in the Odiel, with redox potentials of 605.30 mV and 513 mV, for the Tinto and Odiel, respectively. With respect to metalloid and metal concentrations, the following average values were obtained in the Tinto: As 43.97 μg $L^{-1}$; Cd 99.11 μg $L^{-1}$; Cu 25.32 mg $L^{-1}$; Fe 361.12 mg $L^{-1}$; Zn 19.62 mg $L^{-1}$; and; Mn 9.99 mg $L^{-1}$; while in the Odiel, average concentrations were considerable lower: As 0.39 μg $L^{-1}$; Cd 34.65 μg $L^{-1}$; Cu 4.10 mg $L^{-1}$; Fe 5.34 mg $L^{-1}$; Zn 9.65 mg $L^{-1}$, and; Mn 7.65 mg $L^{-1}$.

## Correlation Matrix

Table 3 presents the Pearson correlation coefficient (R) for pairs of variables in both rivers. Using the values 0.6 and −0.6 as thresholds for high correlations, it is possible to detect some distinct tendencies. First, pH and redox potential were positively associated. The same applies to Cu, Fe, Zn, and Mn. On the other hand, in the Odiel River, pH and redox potential were not significantly correlated and EC was positively correlated with Cd, Cu, Zn, and Mn, which was not observed in the Tinto. Also, there was no correlation between Fe and other metals in the Odiel River, with the exception of the positive correlation observed with Cd. There were also positive associations between variables in the two rivers, such as pH and EC in the Tinto with pH and EC, respectively, in the Odiel.

## Cluster Analysis

Cluster analysis groups variables according to their degree of affinity. Applying the Euclidean Ward method generates a dendrogram plot with all of the variables of both rivers (Fig. 2), and reveals two main groupings. The first consisted of redox potential, Fe, Cu, As, pH, Mn, and Zn in the Odiel River, plus the Mn, redox potential, and pH of the Tinto River. The other group comprises EC, Cd, and $SO_4$ from Odiel together with EC, As, Cu, Fe, Cd, Zn, and $SO_4$ from Tinto and rainwater. Regarding the first group, the strongest association was between the redox potential and Fe with Mn, Cu, and As from the Odiel River. The second

**Table 3** Correlation matrix

| | pH T | Cond T | Redox | As T | Cd T | Cu T | Fe T | Zn T | Mn T |
|---|---|---|---|---|---|---|---|---|---|
| pH T | | | | | | | | | |
| Cond T | −0.3683 | | | | | | | | |
| | 0.0001 | | | | | | | | |
| Redox T | **0.6145** | −0.4273 | | | | | | | |
| | **0.0000** | 0.0000 | | | | | | | |
| As T | 0.0349 | 0.1478 | −0.0642 | | | | | | |
| | 0.7199 | 0.1269 | 0.5093 | | | | | | |
| Cd T | −0.0399 | 0.2645 | −0.1252 | 0.2917 | | | | | |
| | 0.6819 | 0.0057 | 0.1965 | 0.0022 | | | | | |
| Cu T | −0.0165 | 0.3911 | 0.0203 | −0.0956 | 0.1854 | | | | |
| | 0.8651 | 0.0000 | 0.8348 | 0.3249 | 0.0547 | | | | |
| Fe T | 0.0438 | 0.1862 | 0.2572 | −0.3132 | −0.2490 | **0.7052** | | | |
| | 0.6529 | 0.0536 | 0.0072 | 0.0010 | 0.0094 | **0.0000** | | | |
| Zn T | −0.0045 | 0.3434 | 0.0423 | −0.0704 | 0.1483 | **0.8928** | **0.7056** | | |
| | 0.9632 | 0.0003 | 0.6641 | 0.4693 | 0.1257 | **0.0000** | **0.0000** | | |
| Mn T | 0.0446 | 0.3869 | 0.0865 | −0.0788 | 0.0913 | **0.8257** | **0.6584** | **0.8432** | |
| | 0.6464 | 0.0000 | 0.3734 | 0.4176 | 0.3474 | **0.0000** | **0.0000** | **0.0000** | |
| SO4 T | 0.0196 | 0.1724 | 0.0915 | 0.0605 | 0.0920 | 0.1808 | 0.0688 | 0.2415 | 0.2769 |
| | 0.8405 | 0.0744 | 0.3456 | 0.5338 | 0.3438 | 0.0612 | 0.4794 | 0.0118 | 0.0037 |
| pH O | **0.7133** | −0.4057 | **0.6438** | −0.1922 | −0.3044 | 0.0021 | 0.2448 | −0.0236 | 0.0179 |
| | **0.0000** | 0.0000 | **0.0000** | 0.0463 | 0.0014 | 0.9825 | 0.0107 | 0.8088 | 0.8540 |
| Cond O | −0.2301 | **0.7553** | −0.2860 | 0.1679 | 0.2739 | 0.2852 | 0.0803 | 0.2297 | 0.2770 |
| | 0.0166 | **0.0000** | 0.0027 | 0.0825 | 0.0041 | 0.0028 | 0.4085 | 0.0168 | 0.0037 |
| Redox | 0.1605 | −0.0495 | 0.2091 | 0.1404 | 0.2748 | 0.0681 | −0.2023 | −0.0017 | 0.0007 |
| | 0.0970 | 0.611 | 0.0299 | 0.1472 | 0.0040 | 0.4838 | 0.0357 | 0.9863 | 0.9944 |
| As O | 0.1295 | 0.1054 | 0.0357 | −0.1356 | 0.0018 | −0.0025 | −0.0361 | −0.0083 | 0.0674 |
| | 0.1817 | 0.2776 | 0.7141 | 0.1619 | 0.9038 | 0.9799 | 0.7111 | 0.9318 | 0.4881 |
| Cd O | −0.1596 | 0.4713 | −0.3094 | 0.2311 | 0.4236 | 0.1964 | −0.1796 | 0.1699 | 0.1217 |
| | 0.0990 | 0.0000 | 0.0011 | 0.0181 | 0.0000 | 0.0417 | 0.0682 | 0.0787 | 0.2097 |
| Cu O | −0.0173 | 0.3383 | 0.0435 | 0.3369 | 0.4834 | 0.0271 | −0.1906 | 0.0173 | −0.0426 |
| | 0.8588 | 0.0003 | 0.6551 | 0.0004 | 0.0000 | 0.7823 | 0.0482 | 0.8592 | 0.6619 |
| Fe O | −0.1631 | 0.0705 | −0.1022 | −0.1674 | 0.0166 | 0.0810 | −0.0398 | 0.0530 | −0.0974 |
| | 0.0917 | 0.4685 | 0.2987 | 0.0834 | 0.8695 | 0.4048 | 0.6827 | 0.5856 | 0.3159 |
| Zn O | 0.0352 | 0.4364 | −0.1384 | 0.2356 | 0.3343 | 0.2259 | −0.1014 | 0.1857 | 0.1954 |
| | 0.7177 | 0.0000 | 0.1531 | 0.0141 | 0.0004 | 0.0187 | 0.2965 | 0.0543 | 0.0427 |
| Mn O | 0.0069 | 0.4034 | −0.0829 | 0.2308 | 0.2848 | 0.2271 | −0.0267 | 0.2134 | 0.2026 |
| | 0.9431 | 0.0000 | 0.3934 | 0.0163 | 0.0028 | 0.0181 | 0.7840 | 0.0266 | 0.0355 |
| $SO_4$ O | −0.0533 | 0.2048 | 0.1570 | 0.0927 | 0.0455 | 0.2522 | 0.2506 | 0.2706 | 0.2769 |
| | 0.5838 | 0.0335 | 0.1046 | 0.3399 | 0.6476 | 0.0085 | 0.0089 | 0.0046 | 0.0037 |

**Table 3** continued

| | pH T | Cond T | Redox | As T | Cd T | Cu T | Fe T | Zn T | Mn T |
|---|---|---|---|---|---|---|---|---|---|
| Precipitation | 0.1262 | 0.1125 | 0.1162 | −0.0087 | −0.0330 | −0.0306 | 0.1378 | 0.0105 | 0.0373 |
| | 0.1931 | 0.4262 | 0.2311 | 0.9289 | 0.7343 | 0.7536 | 0.1551 | 0.9137 | 0.7013 |

| | SO4 T | pH O | Cond O | Redox O | As O | Cd O | Cu O | Fe O | Zn O | Mn O | SO4 O |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH T | | | | | | | | | | | |
| Cond T | | | | | | | | | | | |
| Redox T | | | | | | | | | | | |
| As T | | | | | | | | | | | |
| Cd T | | | | | | | | | | | |
| Cu T | | | | | | | | | | | |
| Fe T | | | | | | | | | | | |
| Zn T | | | | | | | | | | | |
| Mn T | | | | | | | | | | | |
| SO4 T | | | | | | | | | | | |
| pH O | −0.0819 | | | | | | | | | | |
| | 0.3993 | | | | | | | | | | |
| Cond O | 0.2370 | −0.4385 | | | | | | | | | |
| | 0.0135 | 0.0000 | | | | | | | | | |
| Redox | 0.1539 | **0.0514** | **−0.0394** | | | | | | | | |
| | 0.1118 | **0.5971** | **0.6855** | | | | | | | | |
| As O | 0.1423 | 0.0383 | 0.1109 | 0.1977 | | | | | | | |
| | 0.1419 | 0.6939 | 0.2531 | 0.0403 | | | | | | | |
| Cd O | 0.2877 | −0.4226 | **0.7291** | 0.1414 | 0.0384 | | | | | | |
| | 0.0025 | 0.0000 | **0.0000** | 0.1444 | 0.6928 | | | | | | |
| Cu O | 0.1415 | −0.3168 | **0.5791** | 0.2853 | 0.1305 | **0.6215** | | | | | |
| | 0.1440 | 0.0008 | **0.0000** | 0.0028 | 0.1782 | **0.0000** | | | | | |
| Fe O | 0.0416 | −0.0979 | 0.0609 | 0.1484 | −0.0136 | 0.1052 | 0.1659 | | | | |
| | 0.6690 | 0.3136 | 0.5312 | 0.1253 | 0.8888 | 0.2786 | 0.0862 | | | | |
| Zn O | 0.2371 | −0.1986 | **0.7000** | 0.3232 | 0.1995 | **0.7069** | **0.5324** | 0.1759 | | | |
| | 0.0135 | 0.0394 | **0.0000** | 0.006 | 0.0385 | **0.0000** | **0.0000** | 0.0686 | | | |
| Mn O | 0.2576 | −0.1691 | **0.6700** | 0.2379 | 0.1694 | **0.6459** | 0.4950 | 0.1781 | **0.9416** | | |
| | 0.0071 | 0.0803 | **0.0000** | 0.0132 | 0.0797 | **0.0000** | 0.0000 | 0.0652 | **0.0000** | | |
| $SO_4$ O | 0.2493 | −0.0538 | 0.3100 | −0.0614 | 0.1995 | 0.2030 | 0.1652 | −0.1520 | 0.1687 | 0.2280 | |
| | 0.0093 | 0.5802 | 0.0011 | 0.5277 | 0.0385 | 0.0351 | 0.0876 | 0.1163 | 0.0809 | 0.0176 | |
| Precipitation | 0.0124 | 0.1813 | 0.0253 | −0.1394 | 0.1113 | −0.0421 | −0.1036 | −0.1135 | 0.0617 | 0.0898 | 0.0604 |
| | 0.8984 | 0.0604 | 0.7948 | 0.1501 | 0.2515 | 0.6649 | 0.2862 | 0.2421 | 0.5281 | 0.3555 | 0.5349 |

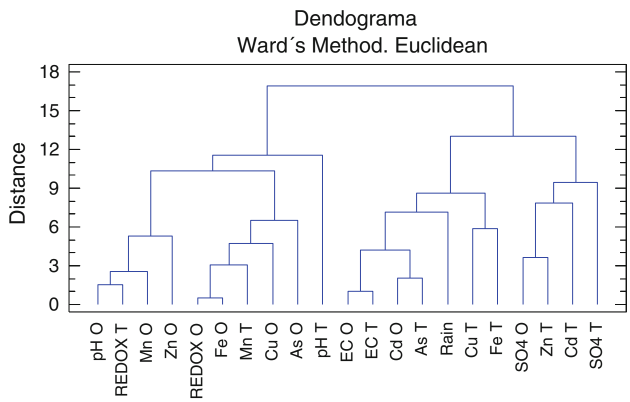



**Fig. 2** *Dendrogram* plot with all the variables of both rivers

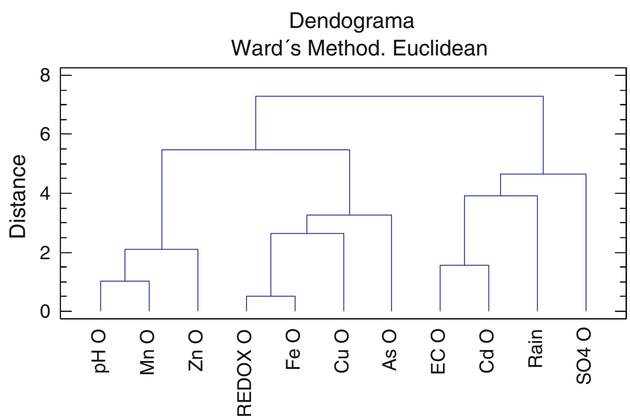



**Fig. 3** *Dendrogram* plot concerning only the variables of Odiel River

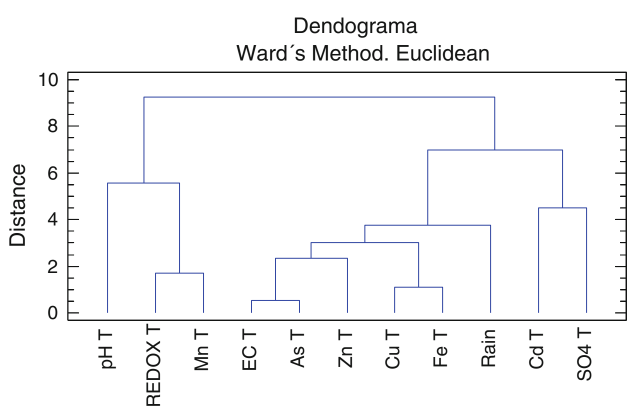



**Fig. 4** *Dendrogram* plot concerning only the variables of Tinto River

group had a strong correlation between the EC in the Odiel and Tinto Rivers.

Figure 3 shows the dendrogram with only the variables of the Odiel River. Once again, there are two main groups of related variables. One involves the redox potential, Fe, Cu, and As with Mn, pH, and Zn, while the other involves the association between EC, Cd, rainwater, and sulfates.

The dendrogram achieved for the variables of the Tinto River (Fig. 4) shows distinctly different associations from those obtained in the Odiel River. One group presents the close relationship between the redox potential with Mn and pH, while the other, distant from the first, contains the rest of the variables.

### Cross-Correlation

Cross-correlation gives information about the relationship between two variables as a function of a time-lag applied to one variable. Figure 5 presents the obtained cross-correlation results. It may be noted that the pairs of variables that have a high correlation coefficient R (Pearson coefficient), i.e., the pH of the Tinto River with the pH of the Odiel River, and the EC of the Tinto River with the EC of the Odiel River, present a higher cross-correlation value for the time-lag $t = 0$. Furthermore, the high value of the cross-correlation between the Cd in both rivers was obtained for a time-lag $t = -2$. For the rest of the variables, there were no significant cross-correlations in any of the studied areas.

### Auto-correlation

Autocorrelation is the cross-correlation of a variable with itself. Figure 6, which appears with the on-line version of this paper, which can be downloaded for free by all journal subscribers, shows the autocorrelation plots for the variables from each river. In these plots, each bar corresponds to 5 days. It can be observed that redox potential in the Odiel River has a memory of 15 days, though in the Tinto River, the memory for this variable is 40 days. In the same way, the memory for the variable As is higher in the Tinto River than in the Odiel River (25 days in the Tinto against none in the Odiel). These are the major differences, since the rest of the variables present very similar memory behavior.

## Discussion

As was observed by Grande et al. (2011a) for the same sampling sites, the statistical summary of the variables shows values that are characteristic of AMD processes. Iron dominated over other metals in the Tinto River, with an average value of 361.1 mg $L^{-1}$, whereas in the Odiel River, the average Fe concentration was 5.34 mg $L^{-1}$. There was a higher rate of precipitation of iron oxyhydroxysulfates in the Odiel River due to more intense neutralization. This also explains, in turn, the higher As concentration (111.8 µg $L^{-1}$) in the Tinto River than in the Odiel River (Grande et al. 2011), since As is strongly

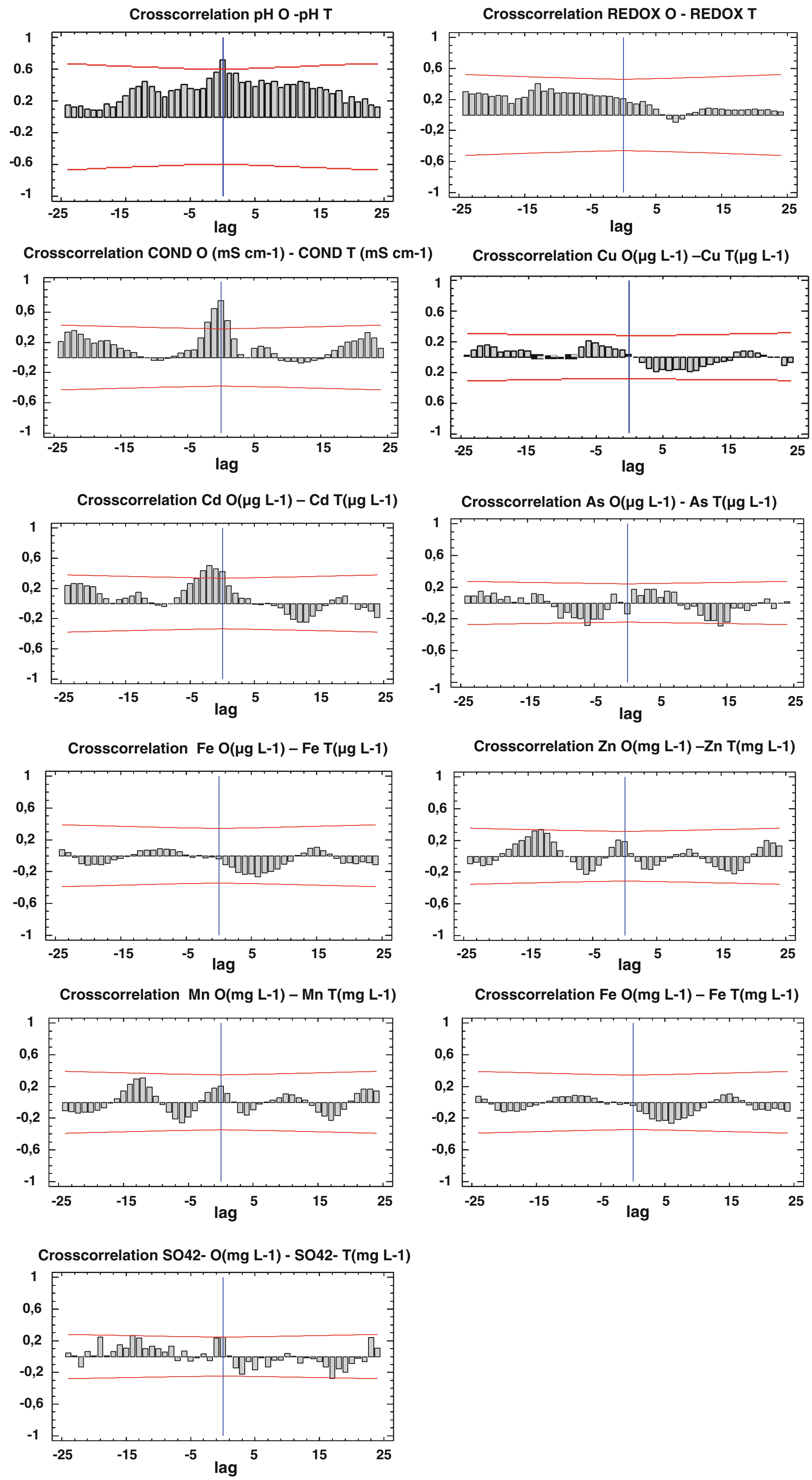



Fig. 5 Crosscorrelation plot

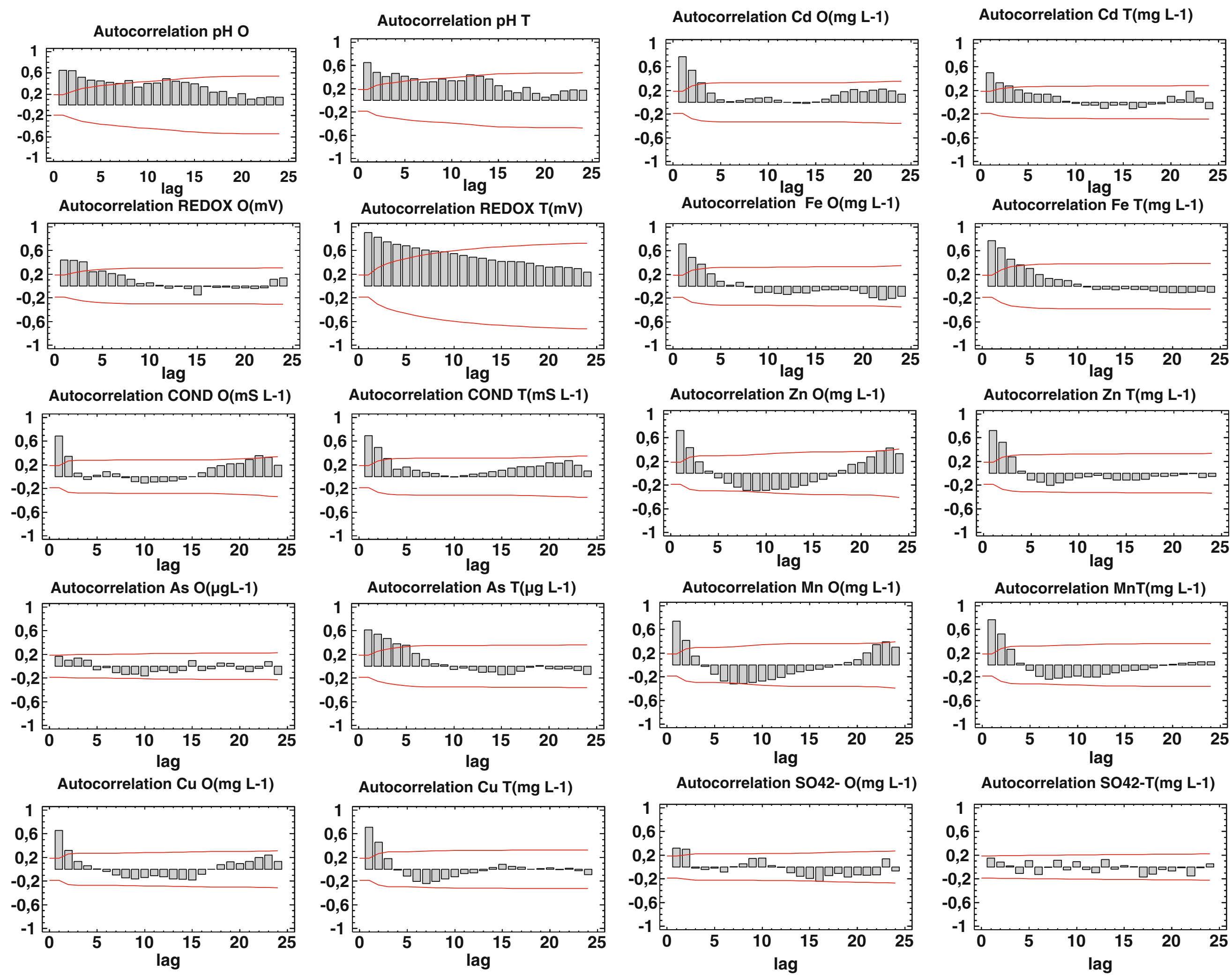



**Fig. 6** Autocorrelation plot

sorbed onto and co-precipitated with Fe oxyhydroxysulfates precipitates (Casiot et al. 2003; Cánovas et al. 2007; Valente et al. 2011).

This process, together with the fact that the Odiel River receives significant contributions from unpolluted water while the Tinto River carries only contaminated water (Sáinz et al. 2005), explains the different behavior of these two rivers in the correlation matrix; in the Tinto River, the Fe is correlated with Cu, Zn, and Mn, which is not true in the Odiel River.

Although both rivers are affected by AMD, the precipitation of metallic compounds in the Tinto River is strongly related to the stability of soluble Fe. On the other hand, in the Odiel, the Fe precipitates mostly upstream, while the higher pH observed near the estuary promotes the retention of metals sorbed onto and co-precipitated with Mn oxyhydroxides and colloids of aluminosilicates. In contrast to the Odiel, in the Tinto River there is a positive correlation between the pH and redox potential, which can be explained by the higher acidity and stronger oxidative power of the Tinto. Therefore, the redox potential autocorrelation results (Fig. 6) shows a memory 2.5 times higher than in the Tinto River. The same can be inferred from cluster analysis, which groups pH and redox potential for the Tinto (Fig. 4), but not for the Odiel River (Fig. 3).

This classical statistical approach gave results that, globally, agree with the conclusions presented by Grande et al. (2011a), in which a fuzzy logic approach demonstrated the distinctive behavior of redox potential in both rivers. These two types of statistical methods indicate that the major difference occurs when the redox potential achieves its maximum value. Under such conditions, the behavior of the rest of the parameters is very different in the Tinto and Odiel rivers.

Of note is the positive correlation that exists between pH (Tinto) and pH (Odiel), and EC (Tinto) and EC (Odiel), which appears highlighted in the correlation matrix (Table 3) as well as in the cross-correlation plots of these parameters (Fig. 5). A time-lag t = 0 indicates a similar behavior of these parameters through time in both rivers. This means that when the pH or EC increase or decrease in the Tinto River, the same is expected to occur in Odiel, with both related to seasonal and mineralogical controls (Cánovas et al. 2007; Nieto et al. 2007).

## Conclusion

Both the Odiel and Tinto Rivers are strongly contaminated by AMD from mines in the IPB. However, the obtained results suggest a distinctive, although somewhat parallel, geochemical behavior. The affinity pattern between parameters differs because the two rivers receive different hydrochemical inputs. In addition to AMD, the Odiel River receives important contributions from non-contaminated catchments. The Tinto River, on the other hand, is the main receptor of drainage from the Rio Tinto mine (one of the largest sulfide ore deposits in the world).

The applied statistical approach revealed that pH and EC present a similar temporal evolution, which point to an identical geochemical signature. This indicates that both systems are affected by a similar type of contamination, proceeding from the same pyritic area.

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