TECHNICAL ARTICLE

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

M. L. de la Torre · J. A. Grande · M. Santisteban ·
T. Valente · J. Borrego · F. Salguero

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.

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).

M. L. de la Torre (✉) · J. A. Grande · M. Santisteban ·
T. Valente · J. Borrego · F. Salguero
Centro de Investigación para la Ingeniería en Minería Sostenible,
Escuela Politécnica Superior de Ingeniería,
Universidad de Huelva, Ctra Palos de la Frontera s/n,
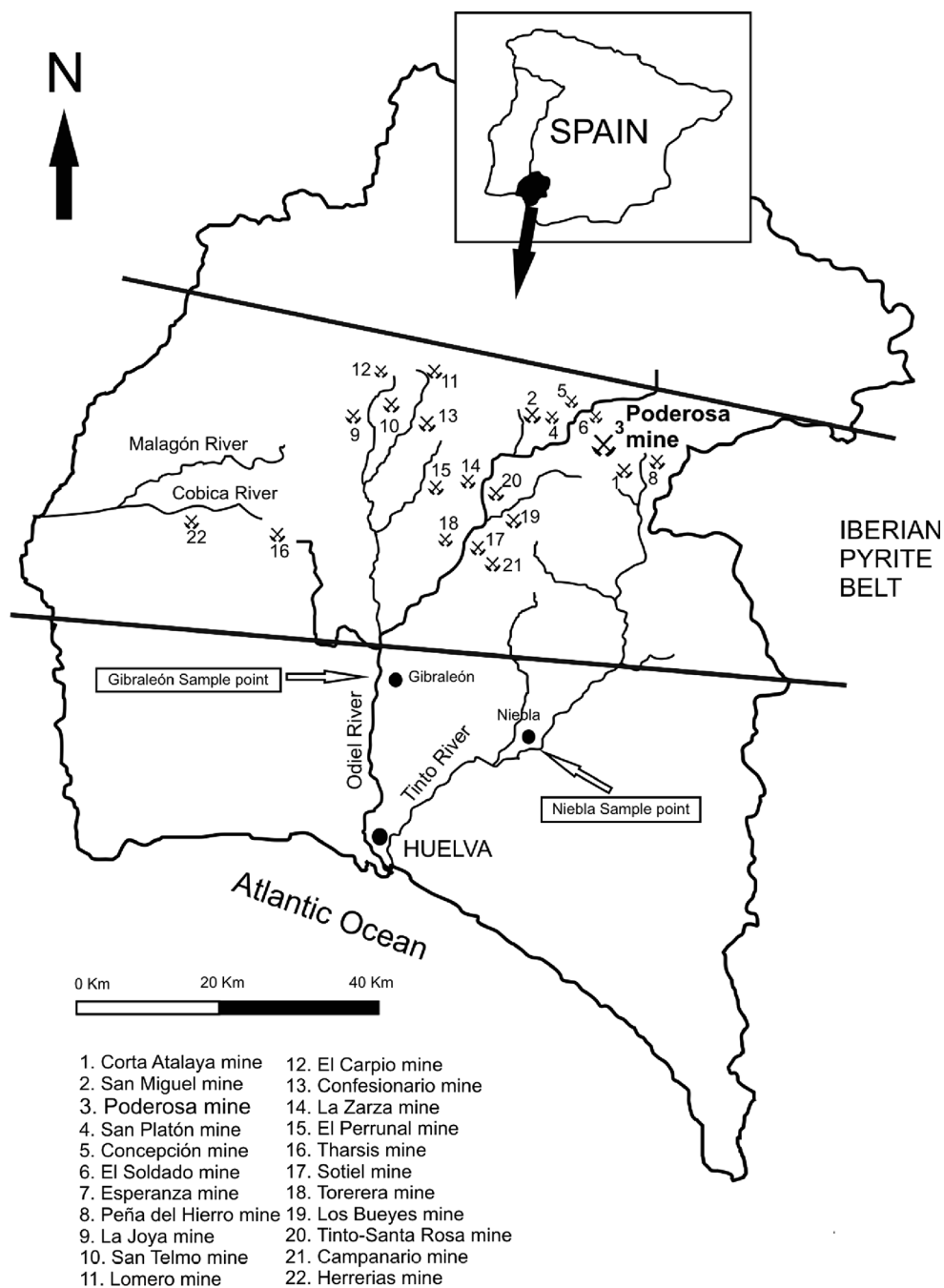21819 Palos, Huelva, Spain
e-mail: mltorre@uhu.es

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

1. Corta Atalaya mine
2. San Miguel mine
3. Poderosa mine
4. San Platón mine
5. Concepción mine
6. El Soldado mine
7. Esperanza mine
8. Peña del Hierro mine
9. La Joya mine
10. San Telmo mine
11. Lomero mine
12. El Carpio mine
13. Confesionario mine
14. La Zarza mine
15. El Perrunal mine
16. Tharsis mine
17. Sotiel mine
18. Torerera mine
19. Los Bueyes mine
20. Tinto-Santa Rosa mine
21. Campanario mine
22. Herrerias mine

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** **0.0000**	−0.4273 0.0000							
As T	0.0349 0.7199	0.1478 0.1269	−0.0642 0.5093						
Cd T	−0.0399 0.6819	0.2645 0.0057	−0.1252 0.1965	0.2917 0.0022					
Cu T	−0.0165 0.8651	0.3911 0.0000	0.0203 0.8348	−0.0956 0.3249	0.1854 0.0547				
Fe T	0.0438 0.6529	0.1862 0.0536	0.2572 0.0072	−0.3132 0.0010	−0.2490 0.0094	**0.7052** **0.0000**			
Zn T	−0.0045 0.9632	0.3434 0.0003	0.0423 0.6641	−0.0704 0.4693	0.1483 0.1257	**0.8928** **0.0000**	**0.7056** **0.0000**		
Mn T	0.0446 0.6464	0.3869 0.0000	0.0865 0.3734	−0.0788 0.4176	0.0913 0.3474	**0.8257** **0.0000**	**0.6584** **0.0000**	**0.8432** **0.0000**	
SO4 T	0.0196 0.8405	0.1724 0.0744	0.0915 0.3456	0.0605 0.5338	0.0920 0.3438	0.1808 0.0612	0.0688 0.4794	0.2415 0.0118	0.2769 0.0037
pH O	**0.7133** **0.0000**	−0.4057 0.0000	**0.6438** **0.0000**	−0.1922 0.0463	−0.3044 0.0014	0.0021 0.9825	0.2448 0.0107	−0.0236 0.8088	0.0179 0.8540
Cond O	−0.2301 0.0166	**0.7553** **0.0000**	−0.2860 0.0027	0.1679 0.0825	0.2739 0.0041	0.2852 0.0028	0.0803 0.4085	0.2297 0.0168	0.2770 0.0037
Redox	0.1605 0.0970	−0.0495 0.611	0.2091 0.0299	0.1404 0.1472	0.2748 0.0040	0.0681 0.4838	−0.2023 0.0357	−0.0017 0.9863	0.0007 0.9944
As O	0.1295 0.1817	0.1054 0.2776	0.0357 0.7141	−0.1356 0.1619	0.0018 0.9038	−0.0025 0.9799	−0.0361 0.7111	−0.0083 0.9318	0.0674 0.4881
Cd O	−0.1596 0.0990	0.4713 0.0000	−0.3094 0.0011	0.2311 0.0181	0.4236 0.0000	0.1964 0.0417	−0.1796 0.0682	0.1699 0.1217	0.1217 0.2097
Cu O	−0.0173 0.8588	0.3383 0.0003	0.0435 0.6551	0.3369 0.0004	0.4834 0.0000	0.0271 0.7823	−0.1906 0.0482	0.0173 0.8592	−0.0426 0.6619
Fe O	−0.1631 0.0917	0.0705 0.4685	−0.1022 0.2987	−0.1674 0.0834	0.0166 0.8695	0.0810 0.4048	−0.0398 0.6827	0.0530 0.5856	−0.0974 0.3159
Zn O	0.0352 0.7177	0.4364 0.0000	−0.1384 0.1531	0.2356 0.0141	0.3343 0.0004	0.2259 0.0187	−0.1014 0.2965	0.1857 0.0543	0.1954 0.0427
Mn O	0.0069 0.9431	0.4034 0.0000	−0.0829 0.3934	0.2308 0.0163	0.2848 0.0028	0.2271 0.0181	−0.0267 0.7840	0.2134 0.0266	0.2026 0.0355
SO4 O	−0.0533 0.5838	0.2048 0.0335	0.1570 0.1046	0.0927 0.3399	0.0455 0.6476	0.2522 0.0085	0.2506 0.0089	0.2706 0.0046	0.2769 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**		
SO4 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
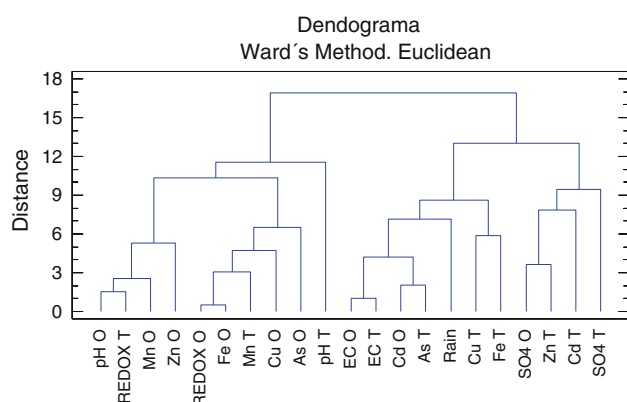
Fig. 2 *Dendrogram* plot with all the variables of both rivers
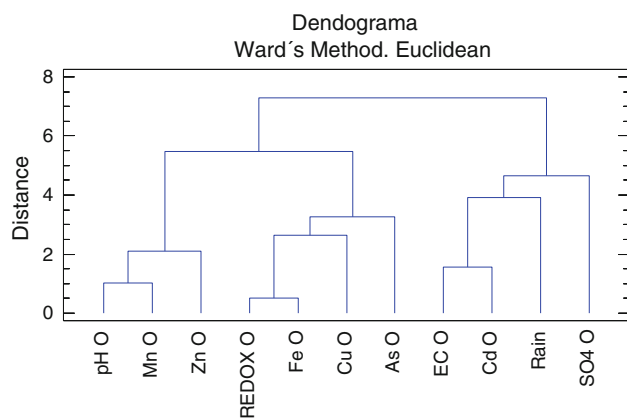
Fig. 3 *Dendrogram* plot concerning only the variables of Odiel River
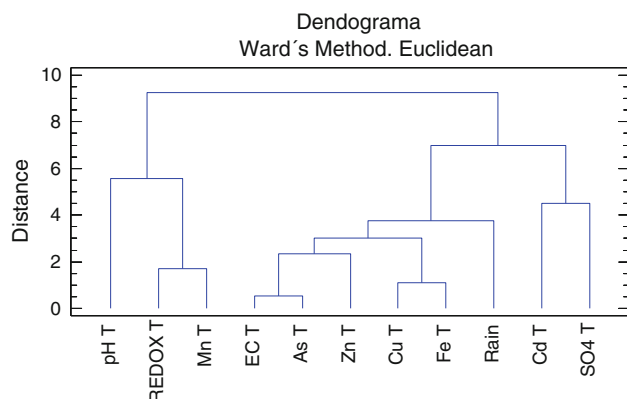
Fig. 4 *Dendrogram* plot concerning only the variables of Tinto River

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.
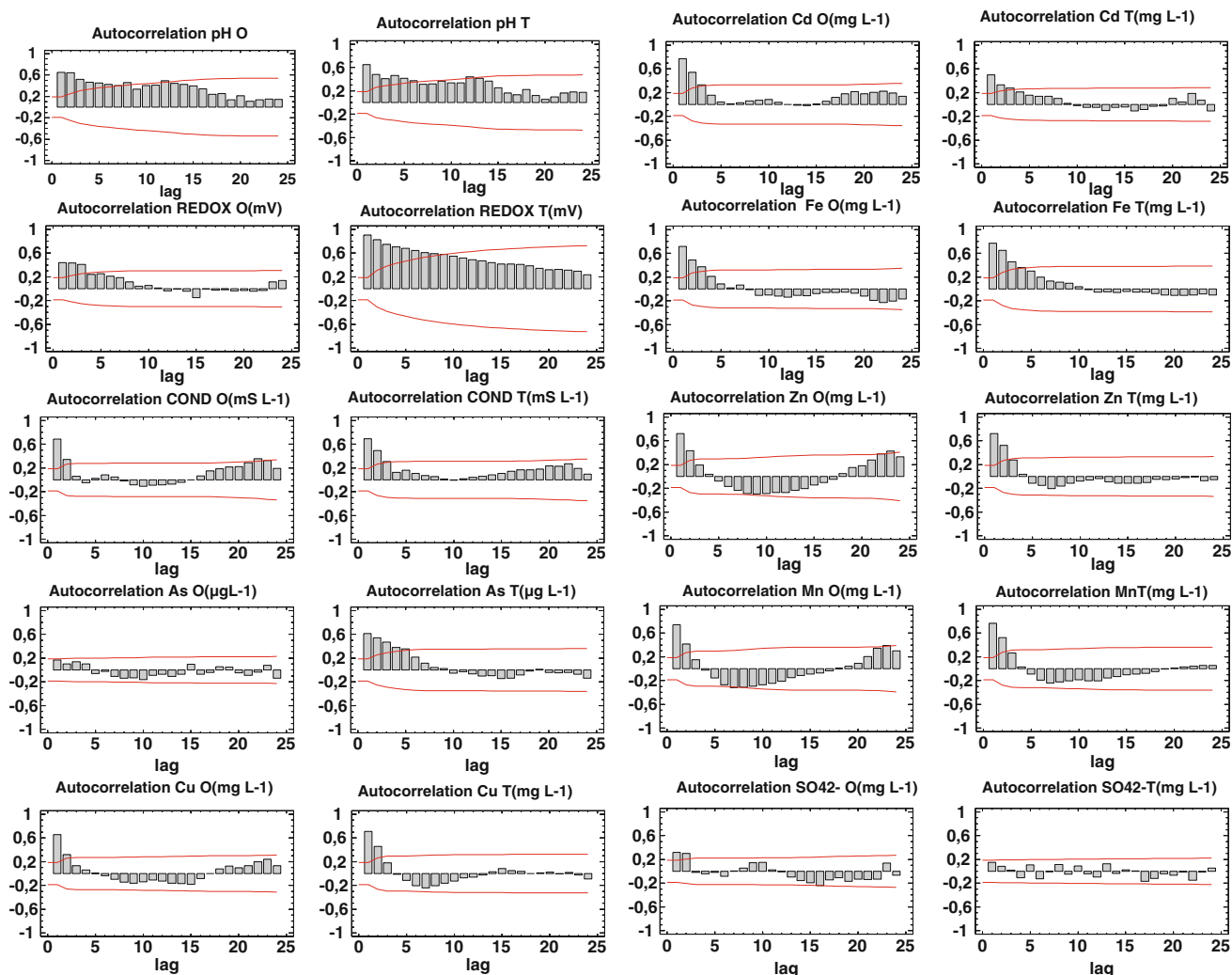
Auto-correlation

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
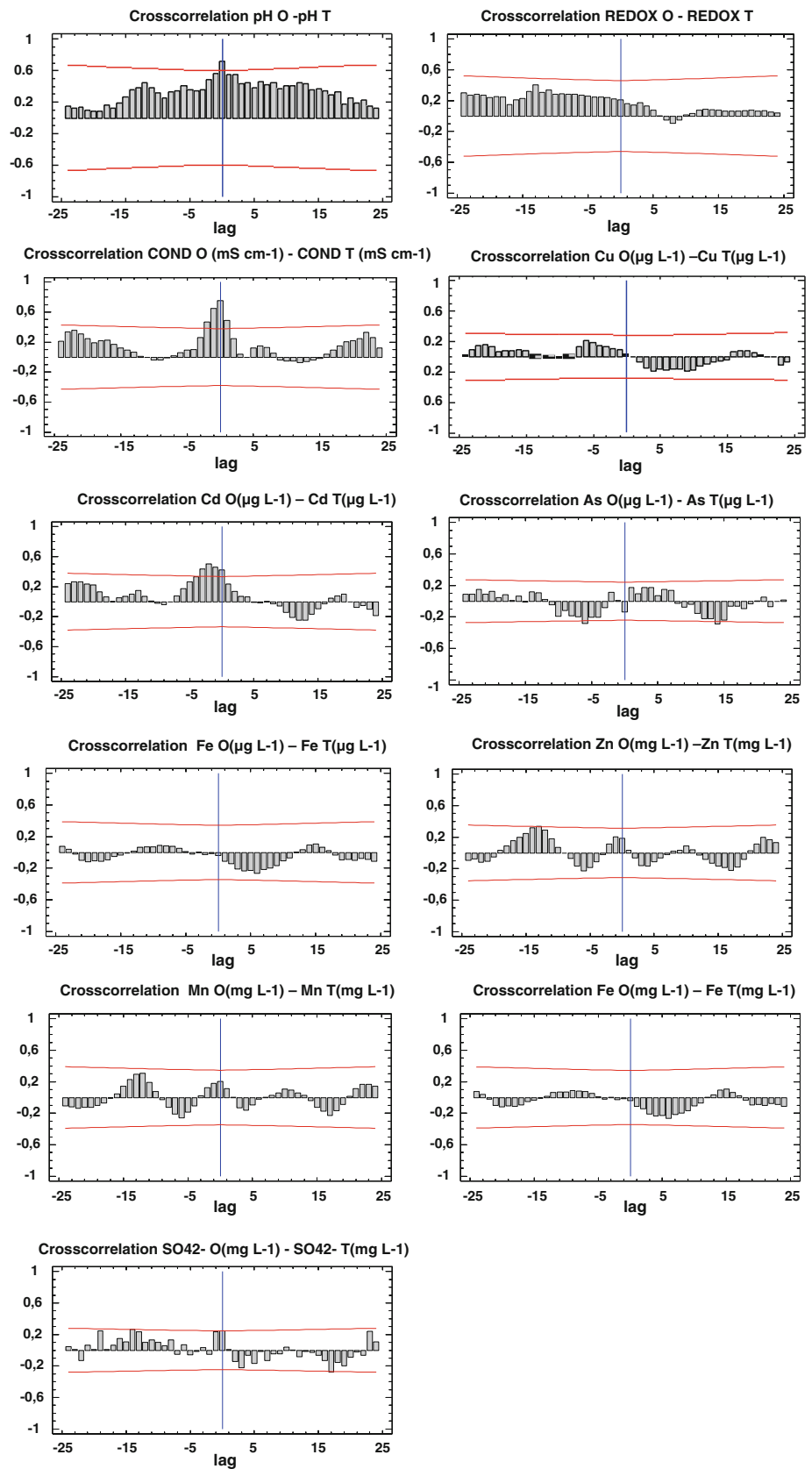
Fig. 6 Autocorrelation plot

sorbed onto and co-precipitated with Fe oxyhydroxysul-fates 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 oxy-hydroxides 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 auto-correlation 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 demon-strated 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.

References

Aroba J, Grande JA, Andújar JM, de la Torre ML (2007) Application of fuzzy logic and data mining techniques as tools for qualitative interpretation of acid mine drainage processes. Environ Geol 53(1):135–145

Azcue JM (1994) Introducción al tratamiento de Series Temporales. Aplicación a las Ciencias de la Salud, Diaz de Santos

Borrego J (1992) Sedimentología del estuario del Río Odiel, Huelva, S.O. España. PhD thesis, Univ of Sevilla, Spain

Borrego J, Morales JA, de la Torre ML, Grande JA (2002) Geochemical characteristics of heavy metal pollution in surface sediments of the Tinto and Odiel river estuary (southwestern Spain). Environ Geol 41:785–796

Borrego J, Carro B, López-González N, de la Rosa J, Grande JA, Gómez T, de la Torre ML (2011) Effect of acid mine drainage on dissolved rare earth elements geochemistry along a fluvial–estuarine systems: the Tinto–Odiel estuary (SW Spain). Hydrol Res. doi:10.216/nh.2011.012

Braungardt CB, Achterberg EP, Nimmo M (1998) Behaviour of dissolved trace metals in the Rio Tinto/Río Odiel estuarine system. In: Morales JA, Borrego J (eds) 2nd annual scientific conference in European land–ocean interaction studies, abstract 51

Cánovas CR, Olías M, Nieto JM, Sarmiento AM, Cerón JC (2007) Hydrogeochemical characteristics of the Tinto and Odiel rivers (SW Spain). Factors controlling metal contents. Sci Total Environ 373:363–382

Carro B, López-González N, Grande JA, Gómez T, de la Torre ML, Valente T (2011) Impact of acid mine drainage on the hydrochemical characteristics of the Tinto–Odiel estuary (SW Spain). J Iber Geol 37(1):87–96

Casiot C, Morin G, Bruneel O, PEersonne JC, Leblanc M, Dusquesne C, Bonnefoy V, Elbaz-Poulichet F (2003) Bacterial immobilization and oxidation of arsenic in acid mine drainage (Carnoulès creek, France). Arsenic behaviour in the aqueous phase. Water Res 37:2929–2936

Davis RA Jr, Welty AT, Borrego J, Morales JA, Pendón JG, Ryan JG (2000) Rio Tinto estuary (Spain): 5,000 years of pollution. Environ Geol 39:1107–1116

de la Torre ML, Grande JA, Jiménez A, Borrego J, Díaz Curiel JM (2009) Time evolution of an AMD-affected river chemical makeup. Water Res Manag 23(7):1275–1289

de la Torre ML, Sánchez-Rodas D, Grande JA, Gómez T (2010) Relationships between pH, colour and heavy metal concentrations in the Tinto and Odiel rivers (southwest Spain). Hydrol Res 41(5):406–413

de la Torre ML, Grande JA, Graiño J, Gómez T, Cerón JC (2011) Characterization of AMD pollution in the river Tinto (SW Spain). Geochemical comparison between generating source and receiving environment. Water Air Soil Pollut 216:3–19

Egal M, Elbaz-Poulichet F, Casiot C, Motelica-Heino M, Negrel P, Bruneel O, Sarmiento AM, Nieto JM (2008) Iron isotopes in acid mine waters and iron-rich solids from the Tinto–Odiel Basin (Iberian Pyrite Belt, southwest Spain). Chem Geol 253:162–171

Elbaz-Poulichet F, Morley NH, Cruzado A, Velasquez Z, Achterberg EP, Braungardt CB (1999) Trace metal and nutrient distribution in an extremely low pH (2.5) river-estuarine system, the Ria of Huelva (south-west Spain). Sci Total Environ 227:73–83

Elbaz-Poulichet F, Dupuy C, Cruzado A, Velasquez Z, Achterberg E, Braungardt C (2000) Influence of sorption processes by iron oxides and algae fixation on arsenic and phosphate cycle in an acidic estuary (Tinto River, Spain). Water Res 34(12–15):3222–3230

Elbaz-Poulichet F, Braungardt C, Achterberg E, Morley N, Cossa D, Beckers J, Nomérange P, Cruzado A, Leblanc M (2001) Metal biogeochemistry in the Tinto–Odiel rivers (Southern Spain) and in the Gulf of Cadiz: a synthesis of the results of TOROS project. Contl Shelf Res 21(18–19):1961–1973

EMCBC (1996) The perpetual pollution machine: acid mine drainage. B.C. Mining Control, Canada, pp 1–6

Förstner U, Wittmann GTW (1983) Metal pollution in the aquatic environment. Springer, Berlin

Grande JA (2011) Impact of AMD processes on the public water supply: hydrochemical variations and application of a classification model to a river in the Iberian Pyritic Belt, S.W. Spain. Hydrol Res 42(6):472–478

Grande JA, Borrego J, Morales JA (2000) Study of heavy metal pollution in the Tinto–Odiel estuary in southwestern Spain using spatial factor analysis. Environ Geol 39(10):1095–1101

Grande JA, Borrego J, Morales JA, de la Torre ML (2003a) A description of how metal pollution occurs in the Tino–Odiel Rias (Huelva-Spain) through the application of cluster analysis. Mar Pollut Bull 46:475–480

Grande JA, Borrego J, de la Torre ML, Sáinz A (2003b) Application of cluster analysis to the geochemistry zonation of the estuary waters in the Tinto and Odiel rivers (Huelva, Spain). Environ Geochem Health 25:233–246

Grande JA, Beltrán R, Sáinz A, Santos JC, de la Torre ML, Borrego J (2005a) Acid mine drainage and acid rock drainage processes in the environment of Herrerías Mine (Iberian Pyrite Belt, Huelva-Spain) and impact on the Andevalo dam. Environ Geol 47:185–196

Grande JA, Andújar JM, Aroba J, de la Torre ML, Beltrán R (2005b) Precipitation, pH and metal load in AMD river basins: an application of fuzzy clustering algorithms to the process characterization. J Environ Monit 7:325–334

Grande JA, de la Torre ML, Cerón JC, Beltrán R, Gómez T (2010a) Overall hydrochemical characterization of the Iberian pyrite belt. Main acid mine drainage-generating sources (Huelva, SW Spain). J Hydrol 390:123–130

Grande JA, Andújar JM, Aroba J, Beltrán R, de la Torre ML, Cerón JC, Gómez T (2010b) Fuzzy modelling of the spatial evolution of the chemistry in the Tinto River (SW Spain). Water Resour Manag 24:3219–3235

Grande JA, Andújar JM, Aroba J, de la Torre ML (2010c) Presence of As in the fluvial network due to AMD processes in the Riotinto mining area (SW Spain): a fuzzy logic qualitative model. J Hazard Mater 176(1–3):395–401

Grande JA, Jiménez A, Romero S, de la Torre ML, Gómez T (2010d) Quantification of heavy metals from AMD discharged into a public water supply dam in the Iberian Pyrite Belt (SW Spain) using centered moving average. Water Air Soil Pollut 212:299–307

Grande JA, Jiménez A, Borrego J, de la Torre ML, Gómez T (2010e) Relationships between conductivity and pH in channels exposed to acid mine drainage processes: study of a large mass of data using classical statistics. Water Resour Manag 24:4579–4587

Grande JA, Aroba J, Andujar JM, Gómez T, de la Torre ML, Borrego J, Romero S, Barranco C, Santisteban M (2011a) Tinto versus Odiel: two AMD polluted rivers and an unresolved issue, an artificial intelligence approach. Water Resour Manag 25:3575–3594

Grande JA, de la Torre ML, Cerón JC, Sánchez-Rodas D, Beltrán R (2011b) Arsenic speciation in the Rio Tinto mining area (SW Spain) during a hydrological year. Water Pract Technol. doi:10.2166/WPT.2011.011

Jimenez A (2009) Caracterización de procesos de drenaje ácido de mina en la cuenca del río Cobica. PhD thesis, Univ de Huelva, Spain

Jiménez A, Aroba J, de la Torre ML, Andujar JM, Grande JA (2009) Model of behaviour of conductivity versus pH in AMD water based on fuzzy logic and data mining techniques. J Hydroinf 11(2):147–153

Leblanc M, Morales JM, Borrego J, Elbaz-Poulichet F (2000) 4,500 year-old mining pollution in southwestern Spain: long-term implications for modern mining pollution. Econ Geol 95:655–662

Nieto JM, Sarmiento AM, Olías M, Cánovas CR, Riba I, Kalman J, Delvalls TA (2007) Acid mine pollution in the Tinto and Odiel rivers (Iberian Pyrite Belt, SW Spain) and bioavailability of the transported metals to the Huelva Estuary. Environ Int 33:445–455

Nocete F, Linares JA (1999) Las primeras sociedades mineras en Huelva Alosno. Historia de la provincia de Huelva cap 4:50–64

Nocete F, Álex E, Nieto JM, Sáez R, Bayona MR (2005) An archaeological approach to regional environmental pollution in the south-western Iberian Peninsula related to third millennium BC mining and metallurgy. J Archaeol Sci 32:1566–1576

Nordstrom DK, Alpers CN, Coston JA, Taylor HE, McCleskey RB, Ball JW, Ogle S, Cotsifas JS, Davis JA (1999) Geochemistry, toxicity, and sorption properties of contaminated sediments and pore waters from two reservoirs receiving acid mine drainage. In: USGS WRI, Reston, VA, USA, pp 289–296

Olías M, Cánovas CR, Nieto JM, Sarmiento AM (2006) Evaluation of the dissolved contaminant load transported by the Tinto and Odiel rivers (southwest Spain). Appl Geochem 21:1733–1749

Pérez-López R, Nieto JM, López-Cascajosa MJ, Díaz-Blanco MJ, Sarmiento AM, Oliveira V, Sánchez-Rodas D (2011) Evaluation of heavy metals and arsenic speciation discharge by the industrial activity on the Tinto–Odiel estuary, SW Spain. Mar Pollut Bull 62:405–411

Sáez R, Pascual E, Toscano M, Almodovar GR (1999) The Iberian type of volcano-sedimentary massive sulphide deposits. Miner Depos 34:549–570

Sáez R, Nocete F, Nieto JM, Capitán MA, Rovira S (2003) The extractive metallurgy of copper from Cabezo Juré, Huelva, Spain: chemical and mineralogical study of slags dates to the third millenium B.C. Can Miner 41:627–638

Sáinz A, Grande JA, de la Torre ML, Sánchez-Rodas D (2002) Characterisation of sequential leachate discharges of mining waste rock dumps in the Tinto and Odiel rivers. J Environ Manag 64(4):345–353

Sáinz A, Grande JA, de la Torre ML (2003a) Analysis of the impact of local corrective measures on the input of contaminants from the Odiel River to the ria of Huelva (Spain). Water Air Soil Pollut 144:375–389

Sáinz A, Grande JA, de la Torre ML (2003b) Odiel River, acid mine drainage and current characterisation by means of univariate analysis. Environ Int 29:51–59

Sáinz A, Grande JA, de la Torre ML (2004) Characterization of heavy metal discharge into the river of Huelva. Environ Int 30:557–566

Sáinz A, Grande JA, de la Torre ML (2005) Application of a systemic approach to the study of pollution of the Tinto and Odiel rivers (Spain). Environ Monit Assess 102:435–445

Sanchez-España J, Lópes E, Santofimia E, Aduvire O, Reyes J, Barettino D (2005) Acid mine drainage in the Iberian Pyrite Belt (Odiel River watershed, Huelva, SW España): geochemistry, mineralogy and environmental implications. Appl Geochem 20:1320–1356

Sarmiento AM, Nieto J, Casiot C, Elbaz-Poulichet F, Ega M (2009) Inorganic arsenic speciation at river basin scales: the Tinto and Odiel rivers in the Iberian Pyrite Belt, SW Spain. Environ Pollut 157:1202–1209

Valente T, Gomes CL (2007) The role of two acidophilic algae as ecological indicators of acid mine drainage sites. J Iber Geol 33:147–158

Valente T, Antunes M, Braga MA, Pamplona J (2011) Geochemistry and mineralogy of ochre-precipitates formed as waste products of passive mine water treatment. Geochem Explor Environ Anal 11:103–106