

Acid mine drainage in the Iberian Pyrite Belt: 1. Hydrochemical characteristics and pollutant load of the Tinto and Odiel rivers

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Abstract Acid mine drainage in the Iberian Pyrite Belt is probably the worst case in the world of surface water pollution associated with mining of sulphide mineral deposits. The Iberian Pyrite Belt is located in SW Iberian Peninsula, and it has been mined during the last 4,500 years. The central and eastern part of the Iberian Pyrite Belt is drained by the Tinto and Odiel rivers, which receive most of the acidic leachates from the mining areas. As a result, the main channels of the Tinto and Odiel rivers are very rich in metals and highly acidic until reaching the Atlantic Ocean. A significant amount of the pollutant load transported by these two rivers is delivered during the rainy season, as is usual in rivers of Mediterranean climate regions. Therefore, in order to have an accurate estimation of the pollutant loads transported by the Tinto and Odiel rivers, a systematic sampling on a weekly basis and a high temporal resolution sampling of floods events were both performed. Results obtained show that metal fluxes are strongly dependent on the study period, highlighting the importance of inter-annual studies involving dry and wet years.

Keywords Iberian Pyrite Belt · Acid mine drainage · Tinto and Odiel rivers · Flood events · Ocean metals load

Introduction

Acid drainage is one of the biggest environmental problems caused by mining of sulphide-rich mineral deposit. Acid mine drainage (AMD) is responsible for the pollution and degraded water quality in groundwater, streams, rivers and whole river basins. Johnson and Hallberg (2005) estimated that in 1989, approximately 19,300 km of rivers and 72,000 ha of lakes and reservoirs throughout the world were severely affected by mining effluents. Mine drainage results from the oxidation of pyrite and other sulphide minerals generally associated with coal and metal-bearing mineral deposits. Mine drainage is most often acidic and contains high concentrations of metals and metalloids. In southwestern Spain, thousands of years of mining in the Iberian Pyrite Belt (IPB) (Davis et al. 2000; Leblanc et al. 2000; Nocete et al. 2005) has resulted in enormous metal-rich wastes that seriously degrade two of the most important basins in the Huelva province, the Odiel and Tinto watersheds (Oliás et al. 2004; Sanchez-España et al. 2005; Cánovas et al. 2007; Sarmiento 2008; Sarmiento et al. 2009, 2011). These two rivers discharge into the Gulf of Cadiz. The pollution load transported by these rivers to the ocean has motivated a large number of studies to assess the processes that control the metal fate and fluxes during estuarine mixing (Elbaz-Poulichet and Dupuy 1999; Grande et al. 1999; Borrego et al. 2002; Sainz et al. 2004; Nieto et al. 2007). Oliás et al. (2006) estimated that the Odiel and Tinto rivers transport enormous amounts of dissolved contaminants: 7,922 t/year of Fe, 5,781 t/year of Al, 3,475 t/year of Zn, 1,721 t/year of Cu, 1,615 t/year of Mn and minor quantities of other metals (71 t/year of Co, 27 t/year of Pb, 35 t/year of As, etc.).

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Sarmiento et al. (2009) estimated that the load transported by both rivers represents 3 % of the global gross flux of Cu and 15 % of the Zn, coming mainly from the Odiel load; however, this estimation should also take into account the contribution of intense rainfall events. Most published works on pollutant transport deal with annual budgets without considering the study of rain events. These type of events need to be studied with a high temporal sampling resolution as geochemical and hydrological factors (i.e. dilution, mineral dissolution/precipitation, sorption processes, changes in AMD sources and rainfall distribution) have a great variability during floods. In addition, the interaction of these factors provokes frequently discharge/concentration hysteresis (Evans and Davies 1998) making the study of these events difficult. Some studies have been performed on the Tinto and Odiel rivers which highlighted the importance of these events in metal transport from rivers to oceans (Cánovas et al. 2008, 2010, 2012a). Therefore, the objective of this study is to estimate the flux of metals from the Tinto and Odiel rivers into the Ría of Huelva and the Atlantic Ocean, considering also the contribution of intense rainfall events that are common for rivers in Mediterranean climate regions. This paper reviews the work of our group during the last 10 years on acid mine drainage in the Iberian Pyrite Belt, summarising and updating our previous work that is widespread in several publications since 2004.

Site description

Geology

Most of the Odiel and Tinto basins flow across the IPB (Fig. 1). The IPB extends east to west from Seville Province, across Huelva Province, into Portugal. It is considered to be one of the larger polymetallic massive sulphide deposit in the world with a length of over 200 km, a width of about 40 km and estimated original reserves in the order of 1,700 mt of sulphide ore (Saez et al. 1999). The IPB belongs to the South Portuguese Zone of the Hercynian Iberian Massif and is formed by upper Palaeozoic materials that can be divided into three lithological groups: (1) the Phyllite–Quartzite Group, formed by a thick sequence of shales and sandstones, (2) the volcano–sedimentary complex (VSC), including a mafic–felsic volcanic sequence interstratified with shales and (3) the Culm group where shales, sandstones and conglomerates prevail. The southern part of both rivers flows across Neogene marly sediments from the Guadalquivir Basin. In the northern part of the area, plutonic and metamorphic rocks from the Ossa-Morena Zone also outcrop.

There are many polymetallic massive sulphide deposits (>80) associated with the VSC. Pyrite (FeS₂) is the main mineral in these deposits, together with lower quantities of

sphalerite (ZnS), galena (PbS), chalcopyrite (CuFeS₂), arsenopyrite (FeAsS) and other sulphides that contain minor quantities of Cd, Sn, Ag, Au, Co, Hg, etc. Figure 1 shows several mines draining into the Odiel and Tinto basins.

Hydrology and climatology

Odiel River comes from Sierra de Aracena and Tinto River from Peña del Hierro mine. Both meet in a common estuary, known as the Ría of Huelva. The Odiel River, which is 140 km long, is the longest. The surface of its drainage basin is 2,300 km². Its annual flow has been estimated at about 500 hm³ year⁻¹. The Tinto River (length 100 km, surface of the watershed 720 km²), has an average annual flow of 100 hm³ year⁻¹. Marked variations from this mean occur in both rivers due to the Mediterranean climate, which includes long periods of drought and intense rainy events. The mean annual rainfall in the zone is 812 mm, 50 % of which occurs between October and January.

The Odiel drainage network has a total of 1,149 km of streams. The most important tributaries in the basin are the Olivargas, Oraque and Meca on the right bank and the Agrio and Villar on the left bank. Several reservoirs have been built in the Odiel River basin. The biggest water reservoirs in the basin are Olivargas and Sancho, with a capacity of 29 and 58 hm³, respectively (Fig. 1).

Methodology

Sampling

Several samplings were performed throughout the whole basins at 24 stations in the Odiel River and at ten stations in the Tinto River between 2002 and 2006 (Fig. 1). A total of 266 water samples were collected.

Flood events were monitored in Tinto and Odiel rivers at points T8 and O13 (Fig. 1), respectively, from 2004 to 2006. Samplings were carried out by a Teledyne ISCO® autosampler, with a sample container holding up to 24 bottles and an outlet pipe made of polyethylene. Samples were pumped by a peristaltic pump, with a schedule purge stage between samplings to avoid cross-contamination (Cánovas et al. 2010). Detailed information about rainfall and river flow data during the period of sampling can be seen in Cánovas et al. (2008, 2010, 2012a, b). Pollutant loads were estimated by establishing relationships between flow and element concentrations. When these relationships were not simple to set, the following equation was applied:

$$L_T = \sum \frac{1}{2} (C_{i(n)} + C_{i(n+1)}) Q_{T(n \rightarrow n+1)}$$

where L_T is the total load, C_i the pollutant concentration in sample i and Q_T is the discharge. For detailed information about estimation methods see Olias et al. (2006) and Cánovas et al. (2012a).

All water samples were filtered in field through 0.22 μm Millipore filters fitted on Sartorius polycarbonate filter holders. Samples for cations and metal analysis were acidified in the field to $\text{pH}<2$ with Suprapur HNO_3 (2 %) and then stored in the dark at 4 °C in polyethylene bottles until analysis. Samples collected for alkalinity and anion determinations were filtered but not acidified. Samples for Fe(II) determination were filtered through 0.1 μm , and the Fe(II) was made complex by adding 0.5 % (w/w) of 1,10-phenanthroline chloride solution after buffering to $\text{pH}=4.5$ with an ammonium acetate/acetic buffer (Rodier et al. 1996).

Analytical determinations

Several physicochemical parameters were measured in the field. Temperature, pH and specific conductance were measured using a portable MX300 multimeter (Mettler Toledo). Dissolved oxygen was analysed using a Hanna meter, and redox potential was determined using a meter with Pt and Ag/AgCl electrode (Crison). The pH meter was calibrated using Hanna pH standard buffer solutions (pH 4.01 and pH 7.01) and redox potential was checked using Hanna standard buffer solutions (240 and 470 mV).

Anions were determined by ion chromatography using a Dionex DX-120 fitted with an AS 9-HC of 4×250 mm column and a 4-mm ASRS-ULTRA suppressing membrane. Detection limits were 0.1 mg L^{-1} for fluoride, nitrate and chloride, and 0.5 mg L^{-1} for sulphate. Alkalinity was determined by the titration method (Standard Methods for the Examination of Water and Wastewater no. 2320) with standardised HCl and bromocresol green indicator.

The concentrations of dissolved Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Si, Sn and Zn were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES Jobin-Yvon Ultima2) using a protocol especially designed for AMD samples (Tyler et al. 2004). Analysis was performed at the Central Research Services of the University of Huelva. Multielement standard solutions prepared from single certified standards supplied by SCP SCIENCE were used for calibration. They were run at the beginning and at the end of each analytical series. Certified reference material NIST SRM-1640 fresh-water-type and inter-laboratory standard IRMM-N3 wastewater test material, from the European Commission Institute for Reference Materials and Measurements, were also used to analyse the samples. Detection limits were calculated by average, and standard deviations, from ten blanks. Detection limits were as follows: 200 $\mu\text{g L}^{-1}$ for Al, Fe, Mn, Mg, Na,

K and Si; 500 $\mu\text{g L}^{-1}$ for Ca; 50 $\mu\text{g L}^{-1}$ for Zn; 5 $\mu\text{g L}^{-1}$ for Cu; 2 $\mu\text{g L}^{-1}$ for As and 1 $\mu\text{g L}^{-1}$ for the other trace elements.

Fe(II) was determined using colorimetry at 510 nm with a Shimadzu UVmini-1240 spectrophotometer. The detection limit was 0.3 mg L^{-1} and the precision was higher than 5 %.

Results and discussion

Hydrochemical characteristics in both rivers

Mean chemical composition and range of the AMD-polluted samples for the Odiel and Tinto basins are listed in Table 1. Representative values of AMD-unpolluted samples for both basins are also included (samples O1 and T6, Fig. 1). The results obtained from analysis of the Odiel samples are characterised by large variations of pH (2.2–7.3), electrical conductivity (0.16–16 mS cm^{-1}) and redox potential (253–813 mV). These large variations are the result of the different degree of mixing of AMD-polluted and AMD-unpolluted waters in the drainage basin. The main water course of the Tinto River is the only affected stream in the whole Tinto Basin. These waters have low pH (1.2–3.0) and high redox potential (583–832 mV); however, the electrical conductivity shows large variations (1.3–37 mS cm^{-1}). All samples from two basins show an excellent correlation ($R^2=0.74$; $\rho<0.05$) between pH and redox potential (Fig. 2). The Eh–pH conditions most commonly found in these waters were acidic and oxidising; however, the Tinto samples are more acids and oxidants in comparison with the Odiel waters.

In the Odiel basin mean concentrations of the main pollutants are the following: Fe (153 mg L^{-1}), Zn (51 mg L^{-1}), Cu (12 mg L^{-1}), As (0.2 mg L^{-1}), Co (1 mg L^{-1}) and sulphate (2,122 mg L^{-1}). By comparison, the conditions in the Tinto River are more extreme than in the Odiel River, with mean sulphate content of 15,164 mg L^{-1} ; Fe, 3,954 mg L^{-1} ; Zn, 90 mg L^{-1} ; Cu, 88 mg L^{-1} ; As, 4.7 mg L^{-1} ; and lower values of Cd, Co, Ni and Pb. The mean contents of pollutants in the Odiel River are much lower than in the Tinto River, especially Fe and As contents (26 and 22 times lower than the Tinto, respectively). Concentrations of Cr, Cu and sulphates are around eight times lower than the Tinto; however, the mean Zn and Ni concentrations are only twice larger in the Tinto than the Odiel River (Table 1).

Most of the samples are high in sulphate concentration with values between 13 mg L^{-1} and 114 g L^{-1} , dependent on the pH values. Sulphate concentration also shows a high correlation ($R^2=0.96$; $\rho<0.05$) with the specific conductance, and with most of the measured metal and metalloids, like Al, Fe, Cu, Co, Zn and As.

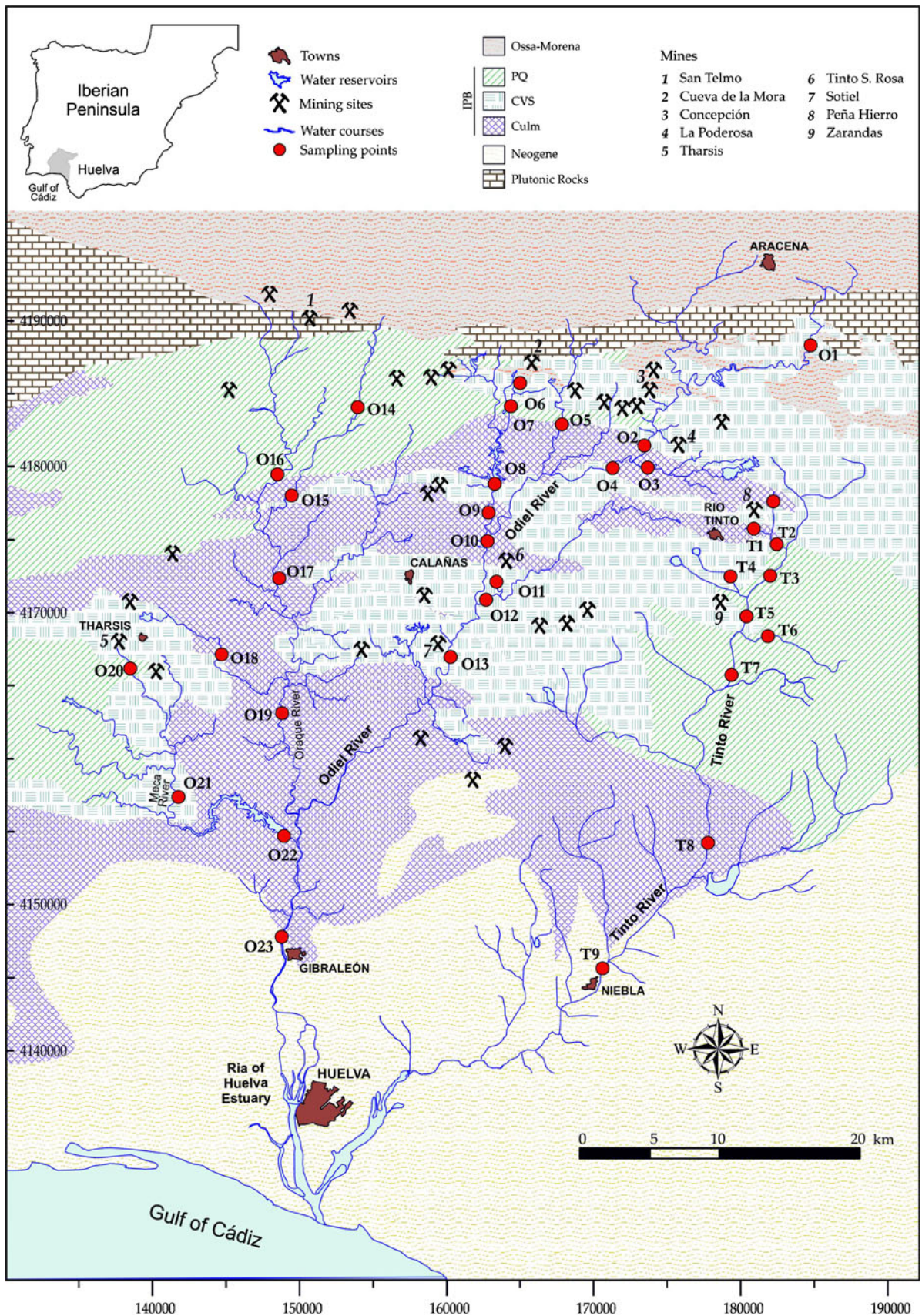


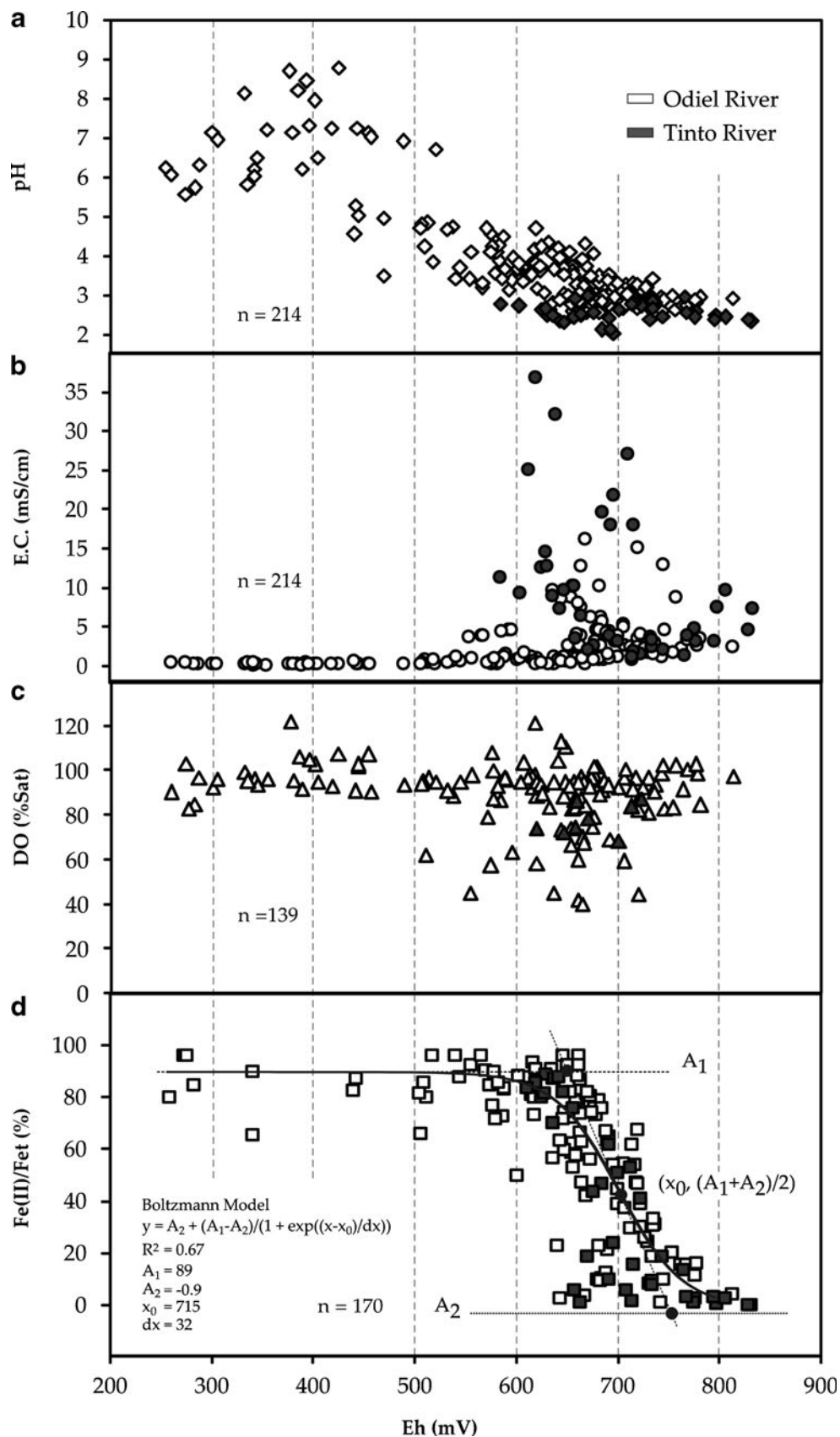
Fig. 1 Geological map of the Odiel and Tinto watersheds, indicating sampling points and the most important mines

Table 1 Average values and range of the measured parameters in the Odiel and Tinto rivers

	Odiel River basin						Tinto River basin					
	Unpolluted			AMD polluted			Unpolluted			AMD polluted		
	stream	<i>n</i>	Mean	Min	Max	SD	stream	<i>n</i>	Mean	Min	Max	SD
pH	8.42	211	3.69	2.17	7.30	1.16	7.09	45	2.38	1.16	2.99	0.40
Eh (mV)	393	189	622	253	813	117	154	39	700	583	832	65.8
CE (mS cm ⁻¹)	0.31	210	2.57	0.16	16.2	3.13	0.11	45	10.1	1.13	36.8	9.05
OD (% sat)	–	146	88.9	19.5	122	15.1	93.0	8	78.3	68.5	87.4	6.99
Al (mg l ⁻¹)	bdl	195	103	bdl	1,140	186	–	41	519	18.0	2,885	617
As (µg l ⁻¹)	2.74	197	215	bdl	4,270	634	bdl	44	4,658	bdl	45,245	10,580
Ca (mg l ⁻¹)	28.8	194	81.6	4.27	454	93.1	3.80	34	154	10.9	458	114
Cd (µg l ⁻¹)	bdl	195	136	bdl	1,323	238	bdl	42	556	bdl	2,913	636
Co (µg l ⁻¹)	8.91	195	965	bdl	12,459	2,022	bdl	43	4,470	142	24,248	5,460
Cr (µg l ⁻¹)	bdl	195	17.7	bdl	240	40.6	bdl	42	145	bdl	826	210
Cu (mg l ⁻¹)	bdl	195	11.7	bdl	140	20.5	bdl	42	88.4	4.80	379	101
Fe (mg l ⁻¹)	bdl	211	153	bdl	1,779	353	bdl	45	3,954	7.60	28,300	6,602
Fe(II) (mg l ⁻¹)	–	159	65.8	bdl	1,560	212	bdl	45	1,105	0.90	10,469	2,544
Fe(III) (mg l ⁻¹)	–	159	82.2	bdl	1,702	241	–	45	2,849	bdl	27,785	6,172
K (mg l ⁻¹)	2.20	194	1.81	bdl	11.0	1.35	0.64	34	4.21	0.10	31.0	6.19
Mg (mg l ⁻¹)	13.0	194	199	1.89	2,769	404	bdl	35	530	24.0	2,353	603
Mn (mg l ⁻¹)	bdl	195	21.9	bdl	201	37.9	bdl	43	48.3	2.20	188	45.1
Na (mg l ⁻¹)	14.8	194	21.4	bdl	107	14.5	10.0	34	56.3	2.09	196	44.9
Ni (µg l ⁻¹)	bdl	195	585	bdl	8,733	1,338	bdl	43	887	47.0	2,687	732
Pb (µg l ⁻¹)	bdl	195	110	bdl	1,425	195	bdl	43	483	bdl	2,719	613
Si (mg l ⁻¹)	3.04	194	12.3	0.28	62.9	12.3	3.10	35	31.0	5.70	73.1	17.8
Zn (mg l ⁻¹)	bdl	195	51.2	bdl	584	101	bdl	43	90.3	4.60	317	87.2
SO4 (mg l ⁻¹)	22.0	194	2,122	13.3	23,622	3,822	9.60	35	15,164	378	114,322	22,423
Cl (mg l ⁻¹)	16.6	35	15.5	6.58	64.4	10.2	15.0	–	–	–	–	–
HCO3 (mg l ⁻¹)	167	30	30.1	bdl	92.0	25.9	–	–	–	–	–	–
CO3 (mg l ⁻¹)	6.86	–	–	–	–	–	–	–	–	–	–	–

n number of samples, *SD* standard deviation, *EC* electrical conductivity, *bdl* below detection limit

Fig. 2 Relationships between redox potential and a pH (diamond), b specific conductance (circle), c dissolved oxygen (triangle) and d $\text{Fe}^{2+}/\text{Fe}_t$ ratio (square) for the contaminated samples in the Tinto and Odiel rivers (Modified from Sarmiento et al. 2009)



The high acidity generated during the sulphide oxidising process gives rise to accelerated hydrolysis of the other minerals in the waste materials and country rocks, mobilising large quantities of their constituent elements. Concentrations of Al, Ca, Mg and Mn are especially high (e.g. Al 195 mg L⁻¹, Ca 82 mg L⁻¹, Mg 199 mg L⁻¹ and Mn 23 mg L⁻¹ in the Odiel River; Al 519 mg L⁻¹, Ca 154 mg L⁻¹, Mg 530 mg L⁻¹ and Mn 48 mg L⁻¹ in the Tinto River).

Figure 2 shows the relationships between redox potential and pH, specific conductance, dissolved oxygen and Fe²⁺/Fe_t ratio for the contaminated samples in both basins. Sarmiento et al. (2009) observed that the distribution of the Fe species may be described by a Boltzmann model for the Odiel basin samples. Including the Tinto basins samples (black symbols in Fig. 2), the result holds (Fig. 2d). In relation to the composition and physicochemical parameters, four groups of streams affected by AMD can be differentiated based on their origin, level of influence of oxidation of sulphides and extent of neutralisation of the acidity generated.

A first group of samples are from streams strongly affected by oxidation of sulphides and are at or near the AMD sources. These samples are essentially acidic leachates which have not undergone dilution or precipitation processes. They all show similar characteristics in connection with the elements associated to the oxidation of sulphides, carrying high quantities of metals and sulphates, including the highest concentrations of Fe (28 g L⁻¹), Cu (379 mg L⁻¹), Zn (584 mg L⁻¹), Ni (8 mg L⁻¹), Co (24 mg L⁻¹), As (45 mg L⁻¹) and Cd (3 mg L⁻¹). These samples show redox potential between 650 and 750 mV, are extremely acidic (pH below 3), have high specific conductance and have elevated Fe²⁺/Fe_t ratio.

A second group of samples show redox potential higher than 750 mV (Fig. 2). This group of streams is strongly affected by AMD but is not so close to the mining sites. They are strongly oxic and acidic waters (pH below 3). Fe(II) is oxidised to Fe(III), so the ratio Fe(II)/Fe decreases. The specific conductance is elevated but lower than the previous group due in part to precipitation of Fe(III)-containing species.

Samples included in a third group show redox potentials between 650 and 750 mV and dissolved oxygen saturation higher than 60 % (Fig. 2c). These streams are strongly affected by AMD but have undergone dilution and/or neutralisation processes. Carbonate minerals are practically non-existent in the IPB, so the neutralisation is basically due to the dilution by uncontaminated water (Cánovas et al. 2007) and to the hydrolysis of aluminosilicate minerals from the country rocks. In these samples pH increases (up to 4, Fig. 2a), and specific conductance decreases (generally less than 4 mS/cm, Fig. 2b). Fe concentration is moderately low (less than 100 mg L⁻¹), and Fe²⁺/Fe ratio shows large

variations according to the dissolved oxygen saturation (Fig. 2d). The most relevant characteristic of these streams are the high concentrations of Ca, Al, Mg and Mn and relatively low Fe contents, which indicates that significant processes involving the precipitation of Fe compounds have occurred.

The last group of samples shows redox potentials of less than 650 mV. These streams are slightly affected by AMD or are strongly diluted/neutralised. Iron concentration is very low and generally only present as Fe(II). The pH values are close to neutrality, and specific conductance and toxic element concentrations are low.

As it can be observed in Fig. 2, Tinto samples have higher conductivity values and are more acidic than the Odiel samples; however, according to the relationship between redox potentials and dissolved iron species, samples from both rivers show the same distribution pattern.

Figure 3 shows the polluted samples plotted in the Ficklin diagram (Plumlee et al. 1992) for the composition of mine drainages. The Ficklin diagram classifies waters based on their pH and the sum of base metals Zn, Cu, Pb, Cd, Co and Ni. The four types of samples described above represent the different degrees of natural attenuation of AMD (Lambeth 1999). Leachates originating from sulphide oxidation have low values of pH and dissolved oxygen, carrying in solution high quantities of Fe(II) and toxic elements (samples from first group). When water contacts atmospheric oxygen, Fe(II) is oxidised to Fe(III), involving Fe(III) precipitation, so redox potential increases and metal concentration decreases (second group). When these leaches are mixed with uncontaminated waters or neutralised by the interaction with country rocks, the pH increases and the dissolved Fe(III) precipitates (third group). If the dilution/neutralisation processes are strong and pH is near neutrality, most of the Fe and toxic metals precipitate (fourth group).

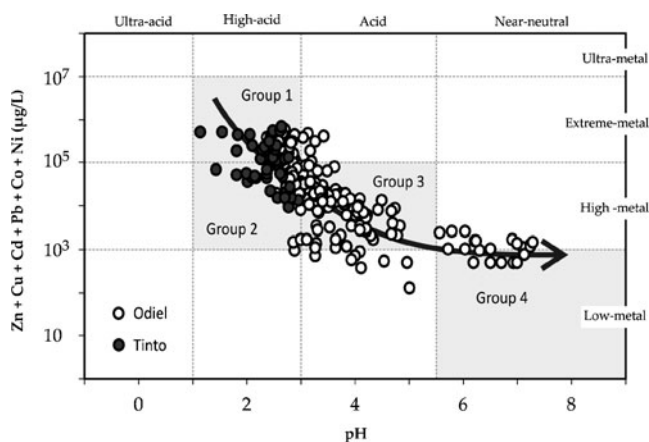


Fig. 3 Ficklin diagram showing the sum of dissolved base metals (Zn, Cu, Cd, Pb, Co and Ni) against pH for contaminated samples from Odiel and Tinto basins (Modified from Sarmiento et al. 2009)

According to this diagram (Fig. 3), in the Odiel Basin, different types of polluted water can be found, from highly acidic waters with extreme metal content to near-neutral waters with low metal content. However, the Tinto river polluted waters are all highly acidic, with a high or extreme metal content.

Dissolved contaminant load transported by the Odiel and Tinto rivers into the Ría of Huelva

Effects of floods on the pollution load assessment

In order to show the importance of flood events monitoring on pollution load estimation, hydrochemical data from Cánovas et al. (2008, 2010, 2012a) of monitored floods under different hydrological conditions are presented. As in other AMD systems (e.g. Keith et al. 2001), dissolved concentrations increase dramatically (Fig. 4b, c) following the first rainfall event of the season due to the progressive dissolution of soluble evaporitic salts and pore waters accumulated during summer on mine areas and the riverbed. Once this mineral store is depleted, a general decrease in concentrations is observed when freshwater dilution processes became increasingly dominant as the winter progresses (Fig. 4e, f). However, not all elements follow the same tendency during flood events as evidenced by Cánovas et al. (2010); a decrease in Na and Sr concentration is observed concomitant to the increase in most elements during the soluble evaporitic salts dissolution. Also, As and Pb did not follow the behaviour of most elements; both elements peaked later than the rest of metals suggesting a geochemical/mineralogical control.

The importance of the Tinto and Odiel rivers as metal sources for the Atlantic Ocean has led to a number of estimates of the dissolved metal loads transported by both rivers (Braungardt et al. 2003; Sainz et al. 2004; Olías et al. 2006). However, despite the large data sets used, these estimates are based at best on a weekly basis and rarely have considered flood events. As previously pointed out in Cánovas et al. (2008), rivers in Mediterranean climate regions, such as the Tinto and Odiel rivers, have alternate long drought periods and short but intense rainfall events during which most of the water discharge and dissolved contaminant and suspended matter transport occur.

Table 2 shows the pollutant load carried by the Tinto and Odiel rivers during two consecutive hydrologic years (2004/2005 and 2005/2006). High-resolution samplings (HRS) during floods allow capturing the sharp hydrochemical changes that takes place in these events. In the case of the Tinto River, the scarcity of rainfalls gave rise to intense wash out processes of soluble salts with the first rainfall after summer. In systematic samplings, based on a weekly basis at best, these data are usually ignored, which underestimated the pollutant loads between 20 and 40 % (Table 2) in both hydrological years. Only both Mn and As estimates provided similar figures.

In the case of the Odiel River, the only flood event monitored (Cánovas et al. 2012a) corresponds to a sampling point placed upstream from that used in synoptic samplings, which does not allow the direct comparison of both sampling approaches. Considering the similar characteristics of both adjacent catchments, synoptic sampling in the Odiel may provide similar underestimation than in the Tinto River. However, both hydrological years were especially dry and the dominant process during monitored flood events was the wash out of soluble salts. When rainfalls are intense along the year, different flood episodes take place and dilution became dominant, and therefore, synoptic samplings may overestimate the pollutant load in both rivers.

The values obtained in the hydrological year 2004–2005 have been compared with the global gross flux based on the compilation made by Gaillardet et al. (2003) for the mean values of trace elements input to estuaries and the ocean by selecting the largest rivers of the world (Table 3). The global gross flux of SO_4^{2-} was based on the result obtained by Meybeck (2003) for the estimation of anthropogenic SO_4^{2-} input to the ocean (Table 3).

The load transported by both rivers represents 0.8 % of the global gross flux of Cu and 2.8 % of the Zn, coming mainly from the Odiel load (Table 3). Estimates performed by synoptic sampling (at a weekly basis) fail to capture flood events and provide lower figures for Zn and Cu (0.5 and 2.0 %, respectively), highlighting the importance of these events in metal fluxes into the ocean.

These calculated metal fluxes are substantially lower than those obtained by Olías et al. (2006). Values of contaminant load for both rivers are notably lower than those reported by Olías et al. (2006); however, the hydrologic years monitored were considerably drier (around 300 and 600 mm, respectively; Table 2) than those considered by these authors (average rainfall of 981 mm from 1995 to 2002). On the other hand, as these estimates were performed on a weekly basis and flood events were not studied in detail, it is reasonable to expect similar errors than those reported in Table 2.

Particulate metal fluxes must also be considered in AMD environments. Cánovas et al. (2012a) detected high total (dissolved + particulate) concentrations of As, Fe, Pb, Cr, Ti, V and Ba during rainy events in the Odiel River due to Fe-rich sediment remobilization, and direct precipitation to a lesser extent. The transported total Fe by the Odiel River was 37 times higher than the dissolved total Fe after rainy events in 2006. Lower values were observed for Pb (seven times higher) and Cr (five times higher), although the most striking finding was recorded for As which was totally transported by particulate matter. These figures highlight the importance of the particulate pollutant load during rainy conditions in AMD-affected river systems. If considered, the very dry season monitored by these authors (maximum

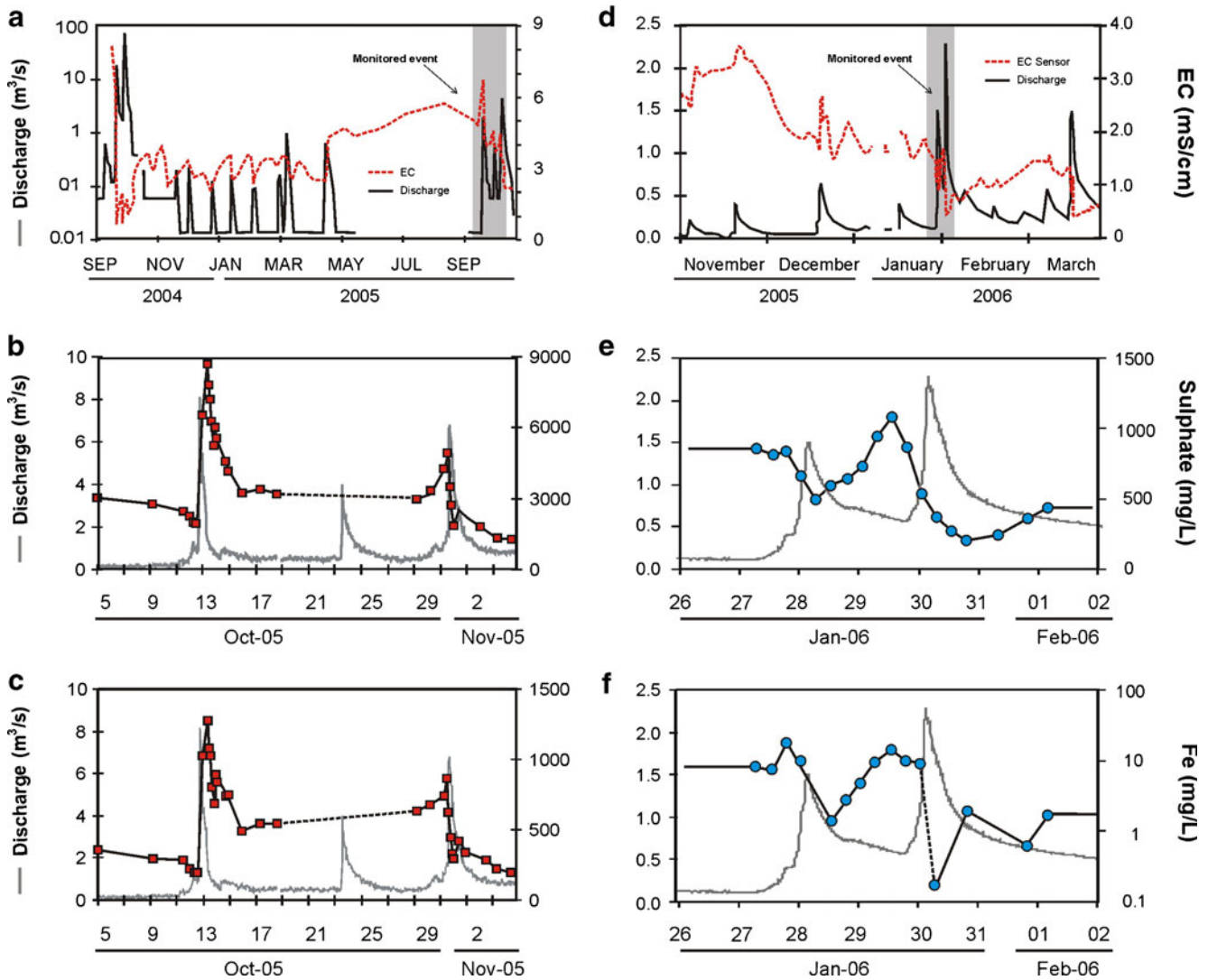


Fig. 4 Flood events studied in the Tinto (a–c) and Odiel (d–f) rivers. Evolution of electrical conductivity (EC) and discharge before and during monitored floods (a, d) and sulphate (b, e) and Fe (c, f)

concentrations during monitored floods in the Tinto (red square) and the Odiel (blue circle) rivers respectively (Modified from Cánovas et al. 2010, 2012a)

discharge of $2.3 \text{ m}^3 \text{ s}^{-1}$), a higher particulate metal load may be expected in more wet seasons.

Conclusions

The Tinto and Odiel rivers drain the central and eastern parts of the Iberian Pyrite Belt. As a result of intense sulphide oxidation processes in the watershed of these two rivers, both of them are acidic and very rich in metals and metalloids. Mean concentrations of the main pollutants are Fe (153 mg L^{-1}), Zn (51 mg L^{-1}), Cu (12 mg L^{-1}), As (0.2 mg L^{-1}) and sulphate ($2,122 \text{ mg L}^{-1}$), for the Odiel River; and Fe ($3,954 \text{ mg L}^{-1}$), Zn (90 mg L^{-1}), Cu (88 mg L^{-1}), As (4.7 mg L^{-1}) and sulphate ($15,164 \text{ mg L}^{-1}$), for the Tinto River.

The four groups of polluted samples can be distinguished in the Tinto and Odiel rivers based on the relationships between redox potential and pH, specific conductance, dissolved oxygen and $\text{Fe}^{2+}/\text{Fe}_t$ ratio, ranging from strongly affected streams near the AMD sources that are highly acidic and have not undergone dilution or precipitation processes to slightly affected or strongly neutralised streams. In the Ficklin diagram for the chemical classification of mine drainages, different types of polluted water can be found in both rivers. In the case of the Odiel River, mine drainages range from highly acidic waters with extreme metal content to near-neutral waters with low metal content; while in the case of the Tinto River, polluted waters are all highly acidic with a high or extreme metal content.

For rivers in Mediterranean climate regions, as is the case of the Tinto and Odiel rivers, a significant amount of the annual

Table 2 Comparison of pollutant annual loads between estimates performed synoptic and high resolution sampling (HRS) during flood events

	Tinto River						Odiel River					
	2004/2005		% Diff		2005/2006		% Diff		2004/2005		2005/2006	
Rainfall (mm)	307				639				290		637	
Type of sampling	Synoptic	HRS ^a			Synoptic	HRS ^b			Synoptic	HRS ^c	Synoptic	HRS ^c
Number of samples	39	53			39	65			40		40	
Pollutant												
Al	474	653	27		605	874	31		1,430	1,816	3,331	4,364
Cu	105	165	37		149	209	28		180	247	442	566
Fe	826	1,312	37		1,717	2,504	31		297	407	668	875
Mn	105	94	-13		61	94	35		253	220	644	869
Sulphate	8,404	9,984	16		11,990	17,249	30		22,154	25,699	59,641	77,533
Zn	104	159	34		148	213	31		366	490	945	1,238
As	0.88	0.79	-11		–	–	–		0.28	0.25	–	–
Cd	0.50	0.77	36		0.74	1.09	32		1.5	2.0	3.7	4.9
Co	3.6	5.0	28		4.3	6.3	31		8.8	11	22	29
Cr	0.10	0.16	33		0.20	0.32	36		0.17	0.23	0.48	0.65
Ni	0.9	1.5	40		1.6	2.4	34		2.8	3.9	9.0	12
Pb	4.4	7.5	41		2.5	3.34	25		0.82	1.2	–	–

^a Estimates including flood data from Cánovas et al. (2008)

^b Estimates including flood data from Cánovas et al. (2010, 2012a)

^c Values corrected from underestimation rate of the Tinto River (see text for explanation)

river discharge can be concentrated in short but intense rainfall events. Therefore, the dissolved contaminant load transported by the Tinto and Odiel rivers into the Ría of Huelva and the Atlantic Ocean is strongly dependent on an accurate estimation of the contribution of the flood events associated with these intense rainfalls. These events should be studied with a high temporal sampling resolution in order to accurately estimate all factors controlling the water chemistry.

Systematic samplings (based on a weekly basis) in the Tinto and Odiel rivers usually do not show the sharp

hydrochemical changes that take place during flood events and generally underestimate the pollutant loads of most elements between 20 and 40 %.

Comparison of the dissolved contaminant load transported by the Tinto and Odiel rivers to the ocean with estimated global gross flux compilations for the largest rivers of the world shows that for the hydrological year 2004–2005, the load transported by both rivers represents 0.8 % of the global gross flux of Cu and 2.8 % of the Zn. These calculated metal fluxes are substantially lower than those obtained in previous

Table 3 Average values of the contaminant load transported by the Tinto and Odiel rivers using both synoptic and high-resolution sampling (HRS), and comparison with global riverine flux estimations of Gaillardet et al. (2003) for the trace elements and of Meybeck (2003) for anthropogenic sulphate

	Total (t/year) Synoptic	Total (t/year) HRS	Global gross flux (kt/year)	% total Synoptic	% total HRS	% Tinto HRS	% Odiel HRS
Al	1,904	2,469	1,200	0.16	0.21	0.05	0.15
Cu	285	412	55	0.52	0.75	0.30	0.45
Fe	1,123	1,719	2,470	0.05	0.07	0.05	0.02
Mn	358	314	1,270	0.03	0.02	0.01	0.02
Sulphate	30,558	35,682	124,000	0.02	0.03	0.01	0.02
Zn	470	649	23	2.05	2.82	0.69	2.13
As	1.16	1	23	0.01	0.00	0.00	0.00
Cd	2.00	3	3	0.07	0.09	0.03	0.07
Co	12.4	16	5.5	0.23	0.30	0.09	0.20
Cr	0.27	0	–	–	–	–	–
Ni	3.68	5	30	0.01	0.02	0.00	0.01
Pb	5.24	9	3	0.17	0.29	0.25	0.04

studies because the hydrologic years monitored were considerably drier (rainfall between 300 and 600 mm) than those considered in the previous studies (mean rainfall of 981 mm), highlighting the importance of long-time studies involving dry and wet years and detailed sampling of flood events in order to accurately calculate mean annual contaminant loads in the Mediterranean climate regions.

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