Metal partitioning and pH-buffering during mixing processes in an estuary strongly affected by acid mine drainage – The Ria de Huelva estuary (SW Spain) ◉

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Abstract

The acidic and metal rich waters of the Odiel and Tinto rivers flow into the Huelva Estuary (SW Spain), where mixing with seawater take place. During these mixing processes intense precipitation of Fe and Al in the fluvial domain of the estuary is observed. Hence, a buffer at pH ranges between 3 and 5.5 is observed, although the spatial location of these buffers is determined by river water/seawater ratio and tides. The information provided by this study is essential to trace the metal fate from rivers affected by AMD to the ocean, particularly to the Gulf of Cádiz and the Mediterranean Sea, which are enriched in metals compared to other seawaters worldwide.

Keywords: Iberian Pyrite Belt, acid rivers, Huelva Estuary, mixing zone, buffer pH

Introduction

Exposure of sulfides to atmospheric conditions leads to contamination of receiving waters by acid mine drainage (AMD), one of the main environmental problems associated with mining of sulfide-bearing ore deposits (Nordstrom and Alpers, 1999). These acid waters are characterized for having a wide range of dissolved constituents and low pH values (Nordstrom 2011). The Iberian Pyrite Belt (IPB, SW Iberian Peninsula) is one the oldest and largest metal-mining district in the world as well as one of the most AMD-affected area (Olias et al., 2006; Nordstrom 2011). Due to its mineral richness, mining activity dates back to Romans and Phoenicians times, but it was especially intense in the last 150 years. Such intense mining activity has left an environmentally impacted area of more than 4800 ha, with around 90 mines (most of them abandoned) and 200 million m3 of mining wastes as a legacy (Grande et al., 2014; Sainz et al., 2004; Cánovas et al., 2010). As a consequence, the Odiel and Tinto rivers, which drain the IPB, are strongly AMD-polluted and present extremely low pH values and high concentrations of metal(oid)s and sulfate (Nieto et al., 2013). Although AMD is usually neutralized by freshwaters downstream of mine sites, there are extreme cases where AMD can cause a direct effect on estuarine systems and coastal areas (Achterberg et al., 2003). An example of this is the Ria of Huelva estuary (SW Spain), which receives the inputs of the acidic (pH 2-4) and metal-rich waters from the Odiel and Tinto rivers. Thus, the estuary is affected by chronic metal pollution and both rivers have been considered to be an important metal contributor to the Gulf of Cádiz (Olias et al., 2006; Nieto et al., 2013). For this reason, this estuary has been focus of much research (e.g. Davis et al. 2000; Elbaz-Poulichet, 2001). However, a detailed characterization of metal behavior and metal fluxes along the estuary upon different hydrological regimes (i.e. dry season, flood events and accidental mine spills) has not been properly addressed. In order to address this issue, systematic field water samplings upon different climate conditions were carried out comprising the sharp pH gradient (3-8) observed along the Ria de Huelva estuary.

Methods

Two field water sampling campaigns upon different climate conditions (i.e. high and low river discharges) were carried out along the estuary (fig. 1) at similar tide conditions. To determine dissolved element concentrations, water samples were collected from a ship, using a Van Dorn bottle (fig. 1a and b). The samples, collected in HDPE bottles previously washed with a 10 % HNO_3 solution, were filtered (0.45 µm), acidified with 1 % ultrapure Nitric Acid and refrigerated until their analysis by iCAP TQ ICP-MS at the HydroSciences laboratory of the University of Montpellier. Estuarine water reference material for trace metals (SLEW-3) and nearshore seawater certified reference material for trace metals (CASS-6) were also analyzed to check the analytical accuracy. In addition, filtered aliquots were used to analyze chloride and sulfate by ion chromatography (Dionex DX-120) at the R+D laboratories of the University of Huelva. Aluminum was determined using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) using a specific protocol for estuarine

and seawaters at the R+D laboratories of the University of Huelva. Temperature, pH, electrical conductivity (EC), and oxidation-reduction potential (ORP) were measured in situ using HANNA HI 98190 and 98192 portable meters. A three-point calibration was performed for both EC (147 µS/cm, 1,413 µS/cm, and 12.88 mS/cm) and pH (4.01, 7.00, and 9.21), while ORP was controlled using two points (240 and 470 mV).

Results and discussion

Three differentiated areas can be defined in the estuary attending to the physicochemical parameters (tab. 1 and fig. 1); the Tinto domain (T8-T1), directly influenced by the Tinto River input; the Odiel domain (O14-O1), where Odiel river waters enter the estuary; and the Padre Santo Channel (C8-C1), where the confluence of both river inputs occurs. A progressive pH gradient is observed along the estuary, with pH values between 3-4 at the fluvial domain and 7-8 at the seawater domain. Electrical conductivity (EC) ranges from around 0.5-0.7 at the most fluvial influence zones to >40 mS cm^{-1} at the
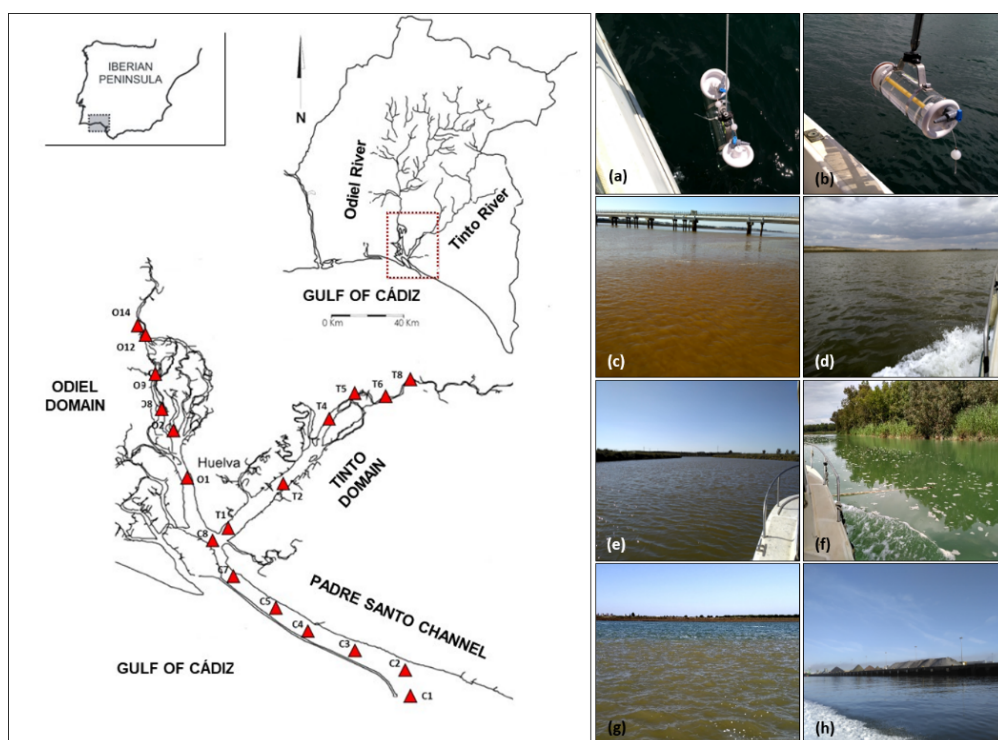

Figure 1 Location map of the Ria of Huelva estuary and sampling points indications (left side). On the right side, photos of the sampling Van Dorn bottle (a, b) and sampling campaign sites, i.e.: Tinto River Domain (c, d), Odiel River Domain (e, f) and Padre Santo Channel (g, h).

channel. Parameter variations can be observed in the estuary associated with the ratio of river water/seawater; for example, lower pH values are observed in the upper zone of the fluvial domain (T8-T5 and O14-12) during low-flow than river high-flow conditions. However, lower pH values are observed in the lower zones of the fluvial domain (T4-T1 and O8-O1) and Padre Santo channel (tab. 1 and fig. 2) during high-flow than during low-flow river conditions.

A similar trend for dissolved Al and Fe concentrations along the estuary can be observed (fig 2). Higher concentrations of both elements were observed at the upper part of the estuary coinciding with the lowest pH values. Higher dissolved Al (27.2±10 mg/L) was observed for low-flow river conditions in both upper estuary zones (fig. 2, left side); while lower Al concentrations (7.2±6 mg/L) were observed during high-flow river conditions. Decreasing concentrations when pH values exceeded 5.5 were observed for the rainy season, being more dramatic in the dry season. At the Padre Santo channel (C8-C1), Al concentrations were close to the detection limit for both low and high-flow river conditions, and only some values (i.e. C7, C4, C5) were reported. Regarding Fe (fig. 2, right side), noticeably higher dissolved concentrations were also observed for low-flow river conditions (May) at the upper part of the Tinto domain (18-49 mg/L; pH <3) than for high-flow conditions (0.8-1.0 mg/L; pH around 4). Concerning the Odiel domain,

slightly higher Fe concentrations were observed in the upper part during low-flow river conditions (i.e. 1-1.6 mg/L) than during high-flow (around 1.1 mg/L). The opposite tendency was also observed for Fe in the lower section of the estuary; higher values were observed during the high-flow conditions in both the Tinto (1.8 to 2.9 mg/L, T4-T1) and Odiel (0.6 to 0.01 mg/L, O8-O1) domains than during low-flow conditions. This inverse metal concentration pattern is explained by the hydrology-mediated chemical characteristics of river waters and the physical topography of the estuary. During low-flow river conditions, Tinto and Odiel river waters show lower flows but higher concentrations than during high-flow conditions. Mixing processes at the upper zone of the estuary are physically controlled by topography, characterized by narrow estuarine channels which limit seawater arrival. Upon these conditions, higher metal concentrations are observed during low-flow river conditions due to the higher concentrations in river water. However, downstream, in the lower section of the estuary, the existence of wide channels allows the contact of large volumes of seawater. Upon these conditions, intense neutralization occurs during low-flow conditions, achieving higher pH values and lower metal concentrations (fig. 2). However, lower pH values and higher metal concentrations are observed during high-flow conditions at the lower section of the estuary (fig. 2) by the buffer effect

Table 1 *Dissolved elements concentrations and selected physicochemical parameters for the two sampling campaigns (high river discharge and low river discharge). Cl-, SO$_4$, Al, Fe, Cu and Zn values are expressed in mg/L whereas As and U are expressed in µg/L. EC means electrical conductivity (mS/cm).*

|	HIGH RIVER DISCHARGE (March)										LOW RIVER DISCHARGE (May)									
Sites	pH	EC	Cl-	SO4	Al	Fe	Cu	Zn	As	U	pH	EC	SO4	Cl-	Al	Fe	Cu	Zn	As	U
T8	4.0	0.7	0.07	171	7.42	0.80	1.37	1.23	0.6	0.7	2.9	2.8	564	0.44	24.46	17.86	7.21	10.46	2.3	3.2
T6	3.9	0.6	0.06	171	7.19	0.68	1.34	1.20	0.8	0.6	2.9	3.9	687	0.71	30.28	34.03	10.14	15.26	3.1	5.0
T5	3.9	0.7	0.08	183	7.78	1.05	1.58	1.36	0.8	0.8	2.9	18.8	1359	5.80	42.57	49.28	14.71	21.00	5.5	12.9
T4	3.7	1.1	0.18	222	9.30	2.86	1.92	1.61	0.7	1.0	4.1	38.4	1863	14.93	10.98	2.46	3.15	3.92	1.6	3.0
T2	5.6	23.8	8.97	1167	0.93	1.80	0.88	1.23	2.3	0.4	7.2	53.3	2289	20.19	n.d.	0.00	0.11	0.44	7.3	2.6
T1	6.3	32.1	14.47	1713	n.d.	0.03	0.18	0.47	1.6	1.9	7.6	56.6	2316	21.82	<0.091	0.01	0.03	0.09	6.3	3.4
O14	4.7	0.5	0.04	147	6.68	1.01	0.94	1.36	0.4	0.6	4.0	8.6	756	6.50	30.15	1.59	4.72	10.70	2.6	5.2
O12	4.7	0.6	0.07	153	6.43	1.11	0.96	1.39	0.6	0.6	4.2	11.3	795	9.50	25.00	1.02	3.94	9.16	2.3	4.7
O9	4.7	0.6	0.12	159	5.79	1.06	0.92	1.38	0.5	0.6	6.2	41.7	1176	14.90	n.d.	0.01	0.38	1.25	1.0	0.8
O8	5.8	14.0	4.57	672	0.68	0.58	0.42	1.23	0.6	0.3	7.5	53.7	2385	20.18	0.14	0.01	0.03	0.19	3.5	2.8
O2	7.0	34.0	12.51	1467	0.01	0.01	0.12	0.56	1.3	1.3	7.5	53.9	2307	20.65	0.21	0.00	0.03	0.15	4.6	2.9
O1	7.1	39.1	15.30	1542	0.06	0.01	0.08	0.41	1.6	1.7	7.7	57.0	2430	21.55	n.d.	0.01	0.02	0.09	5.7	3.3
C8	7.2	42.8	15.40	1704	n.d.	0.01	0.09	0.28	1.9	1.9	7.8	57.5	2436	21.88	<0.047	0.00	0.02	0.05	5.1	3.4
C7	7.0	42.8	16.15	1830	0.1	0.02	0.07	0.32	2.1	2.4	7.7	57.6	2382	21.70	0.14	0.01	0.02	0.06	5.3	3.4
C5	7.7	42.7	18.22	1986	0.15	0.01	0.04	0.20	2.0	2.6	7.8	59.4	2550	22.23	n.d.	0.00	0.01	0.03	4.1	3.3
C4	7.7	43.7	17.32	1881	n.d.	0.00	0.05	0.25	1.9	2.4	7.7	58.5	2571	22.50	0.16	0.01	0.01	0.02	3.6	3.2
C3	7.8	45.7	18.84	2034	n.d.	0.00	0.04	0.18	1.9	2.6	8.0	59.8	2511	21.46	n.d.	0.00	0.01	0.02	2.8	3.1
C2	8.0	53.0	12.23	2286	0.04	0.01	0.02	0.09	1.9	3.0	8.0	60.1	2493	22.44	n.d.	0.00	0.01	0.02	2.9	3.2
C1	8.1	55.6	22.35	2400	n.d.	0.00	0.01	0.03	1.7	3.2	8.0	60.3	2535	22.75	n.d.	0.00	0.00	0.00	1.6	3.1
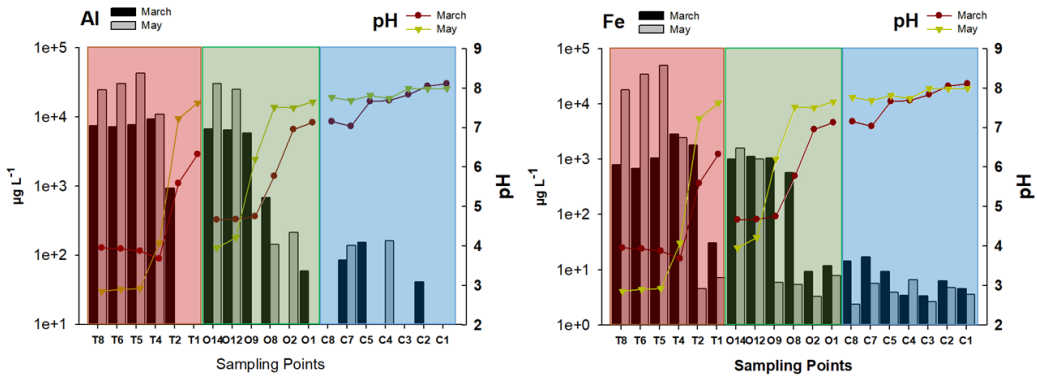
Figure 2 Dissolved concentration of Al (left) and Fe (right) in the different zones of the estuary (i.e. Tinto (reddish shading), Odiel (greenish shading) and Padre Santo Channel (bluish shading) domains) for high (March; black bars) and low (May; gray bars) river discharges. Triangle green (May) and circle red (March) lines represent pH along the estuary for both periods.

exerted by high volumes of acidic river water.

This buffering effect exerted by Fe and Al as a result of the mixture of acidic mine waters with more alkaline waters has been previously studied (e.g. Nordstrom 2011; Carrero et al., 2015) and reported to occur at pH ranges between 2-4 for Fe and 4.5-6 for Al. Although less studied, similar processes take place in estuarine systems affected by AMD as the presented case study. Thus, an intense Fe-Al precipitation zone can be identified in the fluvial domain of the estuary (pH 3.5-5). However, this zone may move depending on the hydrological conditions. For example, this buffer zone is observed to reach T2-T1 and O2 sampling points (fig. 1) during high-flow river conditions, however, both buffer zones are found upstream of these points during low-flow conditions.

The intense precipitation of Fe and Al in the estuarine waters during mixing processes may also affect to other trace metals. As can be seen in figure 3, dissolved Cu and Zn (as well as other elements not shown, e.g. Co, Ni and Cd) decreased their concentrations in the Padre Santo channel (fig. 3). The affinity of both metals to be incorporated in Fe and Al secondary minerals during AMD neutralization has been previously reported (e.g. Carrero et al., 2015). This is evidenced by the high correlations observed in estuarine waters between Fe-Cu, Fe-Zn, Al-Cu and Al-Zn (R2 0.66-0.96) for low and high-flow river conditions. These Fe and Al secondary minerals may also scavenge other elements such as As

and U (e.g. Carrero et al., 2015). However, the behavior showed by these elements differs from that of Fe and Al (fig. 3); a progressive increment of concentration for both elements is observed during high-flow conditions, with maximum concentrations observed in the main channel (fig. 3) while a more erratic evolution is observed during low-flow conditions, with maximum concentrations in T5 for the Tinto domain (fig. 3). This evolution can be explained by desorption processes of both elements from Fe minerals, carried by the river as particulate matter, due to increase of salinity during mixing processes, especially important for U, which forms very stable U-carbonate complexes. At T5 and T4 sampling points, the maximum U peak observed during low-flow conditions (also observed for Fe, Al, Cu and Zn) suggests additional contamination associated with lixiviates from phosphogypsum stack (i.e. wastes from the fertilizer industry with high levels of metals and radionuclides) located in the Tinto river bank. This peak seems to be displaced during low high-flow conditions due to the higher contribution from river water, which dilute this contribution. A similar incremental behavior was observed in a survey carried out between 1997 and 1998, at the same location (Braungardt et al., 2003), that was also attributed to the phosphogypsum deposit.

The European Water Framework Directive (WFD, EU Commission, 2000) urges the adoption of restoration measures in this area
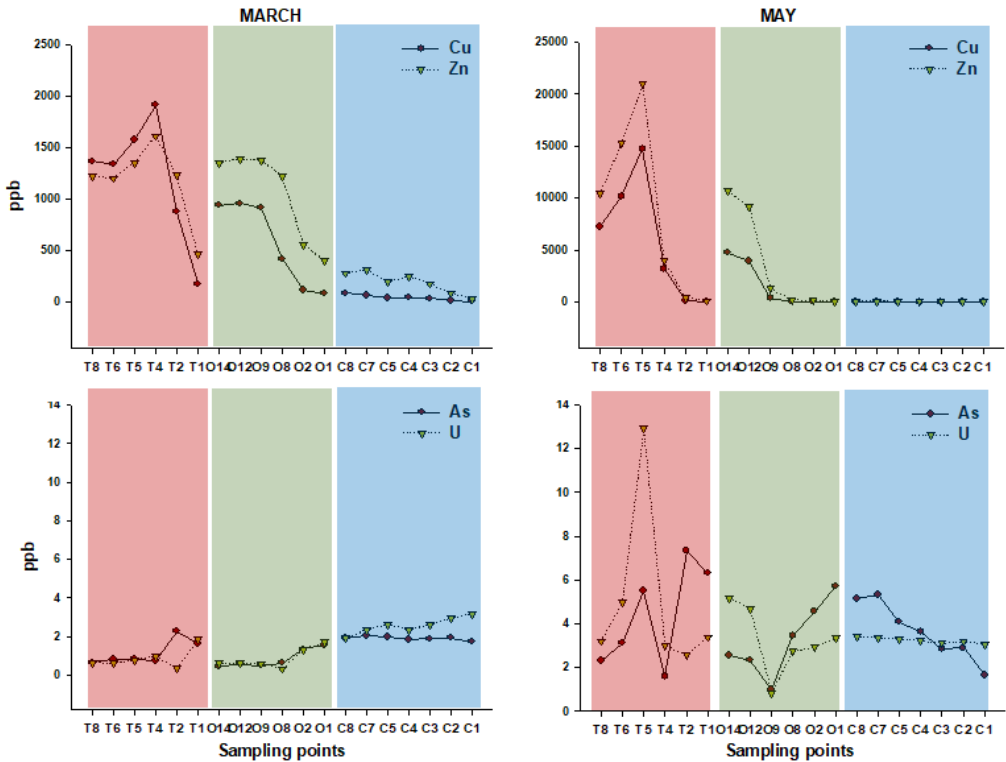
Figure 3 Dissolved Cu, Zn, As and U concentrations for the Ria of Huelva estuary during March (left side) and May (right side) surveys. Reddish, greenish and bluish shadings indicate the Tinto, Odiel and Padre Santo Channel domains, respectively.

to achieve a good chemical and ecological status of the water bodies. In this sense, several passive treatment plants based on dispersed alkaline substrate (DAS) technology (Ayora et al., 2013) have been successfully working at selected acid discharges in the last years. The implementation of other plants and the adoption of other measures will lead to a noticeable improvement of the river water quality (Macías et al., 2017), limiting thus the pollutant load transported from the mines to the estuary.

Conclusions

The Ria of Huelva estuary is a severely AMD-affected system, which receives the inputs of two strongly polluted rivers, the Odiel and Tinto, which drain the IPB. Consequently, enormous concentrations of dissolved elements are transported to the Ria of Huelva estuary and through it to the Atlantic Ocean. The distribution of the contaminants in the estuary is, therefore, highly controlled by the ratio of river water and seawater in the mixing zones.

A buffering effect exerted by Fe and Al as a result of the mixture of the acidic mine waters with more alkaline waters (i.e. seawater) take places in the estuarine system. Thus, an intense Fe-Al precipitation zone can be identified in the fluvial domain of the estuary (pH 3.5-5), for both Odiel and Tinto systems. However, this zone shifts spatially along the estuary depending on the hydrological conditions. For example, this buffer zone is moved downstream during high-flow river conditions, while both buffer zones are found at the more fluvial-influenced zones of the estuary in low-flow conditions. The intense precipitation of Fe and Al also affects to other trace metals. Hence, decreasing dissolved concentrations of elements such as Cu and Zn are observed in the estuary in line with the higher seawater contribution (i.e. higher salinity and pH values). Conversely, progressive As and U concentration increments observed in the Padre Santo channel suggest desorption

processes associated with increase of salinity during mixing processes.

Even though intense precipitation processes were observed in the estuary, most conservative elements (e.g. Cd, Co, Ni) may be yet transported in the dissolved form throughout the estuary reaching the littoral waters. On the other hand, the intense precipitation of Fe and Al minerals along the estuary may lead to increasing levels of metal-rich particulate matter which could cross the estuary until final deposition in the littoral, and therefore it should be studied. In this sense, the spatial variation of pollution in the different sedimentary environments of the estuary and littoral zones, determining the link between the metallic content and the sediment grain size and mineralogical properties should be also assessed in future works. In addition, a reduction of the pollutant load is expected due to restoration measures foreseen in the near future at the mining areas within the actions required by the WFD.

Acknowledgements

References

Achterberg EP, Herzl VM, Braungardt CB, Millward GE (2003) Metal behaviour in an estuary polluted by acid mine drainage: the role of particulate matter. Environmental Pollution 121(2):283-292

Ayora C, Caraballo MA, Macias F, Rötting TS, Carrera J, Nieto JM (2013) Acid mine drainage in the Iberian Pyrite Belt: 2. Lessons learned from recent passive remediation experiences. Environmental Science and Pollution Research 20(11): 7837-7853.

Cánovas CR, Olías M, Nieto JM, Galván L (2010) Wash-out processes of evaporitic sulfate salts in the Tinto river: Hydrogeochemical evolution and environmental impact. Applied Geochemistry 25(2):288-301

Carrero S, Pérez-López R, Fernandez-Martinez A, Cruz-Hernández P, Ayora C, Poulain A (2015) The potential role of aluminium hydroxysulphates in the removal of contaminants in acid mine drainage. Chemical Geology 417:414-423

Elbaz-Poulichet F, Braungardt C, Achterberg E, Morley N, Cossa D, Beckers JM, 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. Cont. Shelf Res. 21: 1961-1973.

Grande JA, Santisteban M, de la Torre ML, Dávila JM, Pérez-Ostalé E (2018) Map of impact by acid mine drainage in the river network of The Iberian Pyrite Belt (Sw Spain). Chemosphere 199:269-277

Grande JA, Valente T, de la Torre ML, Santisteban M, Cerón JC, Pérez-Ostalé E (2014) Characterization of acid mine drainage sources in the Iberian Pyrite Belt: base methodology for quantifying affected areas and for environmental management. Environmental Earth Sciences 71(6):2729-2738

Macías F, Pérez-López R, Caraballo MA, Cánovas CR, Nieto JM (2017). Management strategies and valorization for waste sludge from active treatment of extremely metal-polluted acid mine drainage: A contribution for sustainable mining. Journal of Cleaner Production 141: 1057-1066.

Nieto JM, Sarmiento AM, Cánovas CR, Olias M, Ayora C (2013) Acid mine drainage in the Iberian Pyrite Belt: 1. Hydrochemical characteristics and pollutant load of the Tinto and Odiel rivers. Environmental Science and Pollution Research 20(11):7509-7519

Nordstrom DK (2011) Mine waters: acidic to Circmneutral. Elements 7(6):393-398

Nordstrom DK, Alpers CN (1999) Geochemistry of acid mine waters. In: Plumlee, G.S., Logsdon, M. (Eds.), Society & Economic Geologists 6A, pp. 133–160

Olías M, Cánovas CR, Nieto JM, Sarmiento AM (2006) Evaluation of the dissolved contaminant load transported by the Tinto and Odiel rivers (South West Spain). Applied Geochemistry 21(10):1733-1749

Sainz A, Grande J, De la Torre M (2004) Characterisation of heavy metal discharge into the Ria of Huelva. Environment International 30(4):557-566