

# Dilution Versus Pollution in Watercourses Affected by Acid Mine Drainage: A Graphic Model for the Iberian Pyrite Belt (SW Spain)

J. A. Grande<sup>1</sup> · M. Santisteban<sup>1,2</sup> · E. Pérez-Ostale<sup>1,2</sup> · T. Valente<sup>1,2</sup> ·  
M. L. de la Torre<sup>1</sup> · P. Gomes<sup>1,2</sup> · F. Barrios-Parra<sup>3</sup>

Received: 6 May 2015 / Accepted: 1 November 2017 / Published online: 6 November 2017  
© Springer-Verlag GmbH Germany, part of Springer Nature 2017

**Abstract** The aim of this study was to chemically characterize the water quality impacts of the 88 acid mine drainage (AMD) generating mines in the Spanish sector of the Iberian Pyrite Belt (IPB). This was necessary because the Water Framework Directive of the European Union and the hydrological plans of the Tinto, Odiel, and Piedras river basins require that water quality be improved enough to allow at least some of the rivers in the IPB to sustain healthy fish populations by 2027. The results indicate a clear decrease in metals, arsenic, and sulfate concentrations and increased pH between the AMD-sources and the river channels.

**Keywords** AMD-generating sources · Receiving watercourses · Waste dumps · Metals · Sulfate

## Introduction

The Iberian Pyrite Belt (IPB) is one of the most important metallogenic provinces in the world, and one of the world's largest sulphide deposits (Leistel et al. 1998). This geologic formation is located in southwestern Europe (Fig. 1), extending over 230 km with an average width of 30 km

from northwest of Seville to south of Lisbon. The IPB has been exploited for over 4500 years (Leblanc et al. 2000). Tartessos, Phoenicians, Carthaginians, Romans, and others all mined it, although the greatest boom in production took place in the nineteenth and twentieth centuries, mainly due to British and French interest (Carrasco 2000; Flores Caballero 1983). As a result, there are 88 mines within the Spanish sector of the IPB (Pérez-Ostale et al. 2013) and acid mine drainage (AMD) discharges into the watercourses. There are open pits, wells, galleries, tailing dams, mining facilities, and waste dumps, the latter being the main source of contamination, especially when they were abandoned or improperly closed (Loredo and Pendás 2005). Recently, mining has resumed in the IPB due to the demand for copper in emerging countries (Grande et al. 2014).

Figure 1 shows the river network and the inventoried mines in the IPB. The affected river network includes, as major receptors, the Chanza, Odiel, Tinto, and Guadamar Rivers. Most of the mines are abandoned; only the Cobre las Cruces and Aguas Teñidas mines are operating, though others may reopen.

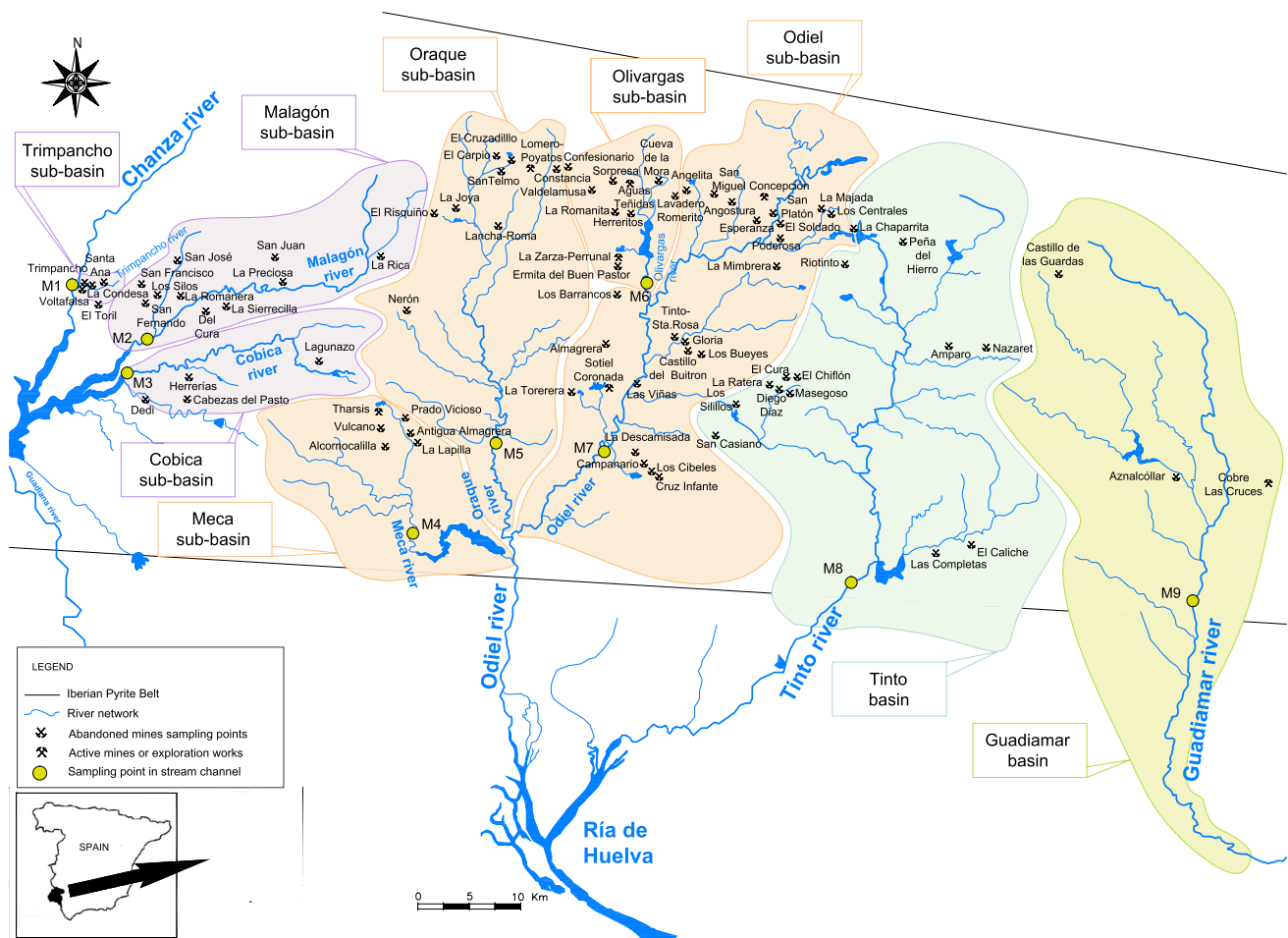
The IPB is a unique AMD-generating source due to the magnitude and ubiquity of the AMD discharges in this metallogenic province. The Water Framework Directive of the European Union and the hydrological plans of the Tinto, Odiel and Piedras rivers basins require that some of the rivers in the area have “a good ecological status” and a water quality that will support fish (salmonids and cyprinids) by 2027. Thus, an accurate inventory of the pollution and an evaluation of the impacts of each mining site in the river network were necessary and a hydrochemical characterization of the mining leachates and receiving streams was performed for the entire province. The cause–effect relationships between processes (namely the significance of the waste dumps as AMD-generating sources) and consequences

✉ J. A. Grande  
grangil@uhu.es

<sup>1</sup> Centro de Investigación para la Ingeniería en Minería Sostenible, Escuela Técnica Superior de Ingeniería, Universidad de Huelva, Ctra. Palos de la Frontera, s/n, 21819 Palos de la Frontera, Huelva, Spain

<sup>2</sup> ICT, Institute of Earth Sciences, Pole of the University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

<sup>3</sup> Environmental Geochemistry and Engineering Laboratory, Universidad Politécnica de Madrid, Alenza 4, 28003 Madrid, Spain



**Fig. 1** Location map showing the river network and the sampling sites

(degree of contamination of the water system, as indicated by pH, sulfate and metal load) were defined at the watershed level.

## Methodology

The AMD-generating sources and the main watercourses were characterized using a sampling network that spanned the entire province. This network comprises two groups of sampling points (Fig. 1). The first group corresponds to the mining leachates. At each mine, a sampling site was established at the base of each waste dump, because they have been shown to be the main sources of AMD (Sáinz 1999; Pérez-Ostale et al. 2013). In general, water upwelling through wells and galleries is negligible for this area. The two operating mines were not included in the sampling network because, within the current legal framework, they must recycle all of the water used in the mining process and obtain a permit for any discharges into the river network.

This requires that they implement water treatment systems; hence, they will not generate AMD.

The second group of sampling points was located in each major watercourse, downstream of the AMD sources, and represents the temporary receiving system. Nine sub-basins were defined under the scope of this work for the Spanish sector of the IPB: Trimpancho, Malagón, Cobica, Meca, Oraque, Olivargas, Odiel, Tinto, and Guadiamar. Although in previous work (Grande et al. 2010a; Sarmiento 2007), the Olivargas sub-basin was not considered to be a sub-basin of the Odiel River, it was treated as such in this study based on the potential hydrogeochemical effects associated with existing mining, i.e. Aguas Teñidas.

A sampling campaign was performed during the hydrological year 2012/2013, in the rainy season; water samples were collected daily in March 2013. This was a critical condition for production of leachate in all of the mined areas, since leaching occurs only briefly after rain at some of the smaller mine waste dumps. The pH, temperature (T), electrical conductivity (EC), and total dissolved solids (TDS) were measured in situ three times consecutively to avoid errors,

using a multi-parametric portable device (CrisonMM40). At each point, two water samples were taken in polyethylene sterilized containers of 100 and 200 mL. Nitric acid at 1% concentration was added to the 200 mL sample, to maintain a pH below 2, to prevent metal precipitation. The other sample was not acidified to allow for subsequent sulfate analysis. The samples were placed at 4 °C in a portable cooler for transportation to the laboratory. There, water samples were filtered with cellulose nitrate filters of 0.45 µm (Sartorius 11406-47-ACN) with a vacuum pump to accelerate flow, and then stored in sealed polyethylene containers in a refrigerator at a temperature between 1 and 4 °C.

A photometer was used to determine the sulfate concentration (Macherey-Nagel Photometer FP-11). Metals and arsenic concentrations were determined using a Perkin-Elmer atomic absorption spectrophotometer (AAS) Analyst model 800 equipped with a flame spray of air-acetylene and a graphite furnace. All reagents used were of analytical grade or supra-pure quality (Merck, Darmstadt, Germany). The standard solutions were Merck Certificate AA. In all of the experiments, Milli-Q (18.2 MΩ cm) water was used. The cause-effect relationships between AMD-source and receiving watercourse were also established for the nine basins and sub-basins. The hydrochemistry of the key points was

graphically represented to illustrate variations in the water properties due to dilution.

## Results and Discussion

Leachates produced in 80 sulfide-rich waste dumps were analyzed, and grouped into the nine defined sub-basins. Table 1 presents the leachate properties. The results do not include six very small mines where no leachates were found at the time of sampling (Nerón, Herrerito, Los Barrancos, Los Centrales, San José, and Nazaret). Also, the two currently operating mines were not included in the sampling since they were not contributing pollutants, as already mentioned. The results indicate that in most cases, the water quality was indicative of an AMD-affected environment, as shown by the mean values for pH (3.51), EC (2224 mg/L), TDS (1501 mg/L), sulfate (1105 mg/L), and metals.

The highest pH was associated with the Alcornocalill mine (7.75), and the lowest with the Riotinto mine (2.01). The latter has waste dumps in two sub-basins, the Odiel and Tinto, and, thus discharges leachates to both rivers. Therefore, two sampling points were used for the Riotinto mine. Maximum values of sulfate (3850 mg/L), EC (41,300 µS/

**Table 1** Hydrochemistry of the mining leachates—range of variation detected for the entire province

Parameter	Maximum	Minimum	Average
pH	7.75–Arcornocalilla	2.01–Riotinto	3.51
EC (µS/cm)	41,300–Riotinto	35–Ermita del Buen Pastor	2224
SO <sub>4</sub> <sup>2-</sup> (mg/L)	3850–Riotinto	20–San José	1105
TDS (mg/L)	26,400–Riotinto	22–Ermita del Buen Pastor	1501
Fe (mg/L)	78.19–La Condesa	0.099–Vulcano	33.37
Cu (mg/L)	73.49–Poderosa	ND–San José	17.27
Pb (mg/L)	3.60–La Rica	ND–(I)	0.22
Zn (mg/L)	75.01–Riotinto	ND–Ermita del Buen Pastor	4.877
Mn (mg/L)	28.74–Riotinto	0.027–Cruz Infante	5.89
Co (mg/L)	12.91–Riotinto	ND–(II)	0.62
Ni (mg/L)	1.63–Almagrera	ND–(III)	0.25
As (mg/L)	4.21–Herrerías	N.D.–(IV)	0.40
Cd (mg/L)	2.54–Riotinto	ND–San Casiano	0.69
Mg (mg/L)	127.30–Trimpancho	0.102–Confesionarios	29.45
Ca (mg/L)	159.70–La Romanera	1.041–Prado Vicioso	23.26
Al (mg/L)	1.19–Cruz Infante	0.016–Dedi	0.55
Sb (mg/L)	3.33–Sotiel Coronada	ND–(V)	0.07

ND: Below the detection limit (0.001 µg/L)

(I): Alcornocalilla, Amparo, Angostura, Castillo de las Guardas, Confesionarios, Constancia, Cruz Infante, Diego Díaz, El Caliche, El Chiflón, El Cruzadillo, La Chaparrita, La Preciosa, Lancha-Roma, Los Cibeles, San Casiano, San José, San Miguel, Sorpresa, Tinto Santa-Rosa

(II): Castillo del Buitrón, Los Bueyes, San Casiano

(III): La Preciosa, San José

(IV): Dedi, Diego Díaz, El Chiflón, El Caliche, El Toril, Fronteriza, La Condesa, Los Silillos, Los Silos, San Fernando, San Francisco, Santa Ana, Tinto Santa-Rosa, Trimpancho, Voltafalsa

(V): Castillo del Buitrón, Los Bueyes

cm), Zn (75.01 mg/L), Mn (28.74 mg/L), Cd (2.54 mg/L), and Co (12.91 mg/L) were obtained at the Riotinto mine. Maximum concentrations of Fe (78.19 mg/L) and Cu (73.49 mg/L) were observed at the La Condesa and Poderosa mines, respectively. The La Rica mine had the highest Pb (3.60 mg/L) concentrations, Almagrera has the greatest Ni levels (1.63 mg/L), and the Herrerias mine had the highest As concentrations (4.21 mg/L). The lowest values were associated with the small mines, where the contaminant load had already been washed by the time of sampling. In most cases, concentrations at these sites were below detection limits. However, in the case of Pb and As, the low concentrations were observed in different areas. This may be due to the low abundance of arsenopyrite, galena, and other polymetallic sulfides in those locations.

The physical–chemical parameters in most of the receiving watercourses are indicative of AMD (Table 2). Metals and arsenic were observed at lower concentrations in the Guadiamar, Olivargas, and Malagón river basins, while maximum contaminant values were found in the Tinto and Meca Rivers. Of course, the pH showed the opposite trend, with the lowest pH in the Tinto River (2.13) and the highest in the Guadiamar River (6.49). The greatest EC and TDS values were observed in the Malagón River (1087  $\mu\text{S}/\text{cm}$  and 695 mg/L, respectively), and the least in the Olivargas River (171  $\mu\text{S}/\text{cm}$  and 110 mg/L, respectively). Sulfate concentrations were highest in the Trimpancho basin (1060 mg/L), and lowest at Malagón (31 mg/L). Therefore, the Meca and Tinto Rivers contained more maximum metal concentrations. However, the Odiel River, well known for its AMD

contamination (de la Torre et al. 2010; Elbaz-Poulichet et al. 2001; Sáinz et al. 2000; Sánchez-España et al. 2006), did not show any maximum value, presumably due to its large flow and dilution from uncontaminated areas (Sáinz et al. 2004).

In general, the results in Tables 1 and 2 were lower than those obtained in other studies about AMD in the IPB, although maintaining a constant proportionality (de la Torre et al. 2011; Jiménez et al. 2009; Sarmiento 2007). This may be because the sampling was performed in the rainy season so that leachates would be obtained from all of the mines. It should be noted that the duration of the leachate discharges depends on the size of the waste dumps. The small ones remain dry most of the year, and leaching occurs only briefly after rain. By contrast, the large dumps discharge leachate for several weeks, and some maintain a drainage flow the entire year (Sáinz et al. 2002).

The relationships between AMD-source and receiving watercourse were established for the nine defined river basins. The results generally show that metal concentrations, arsenic, and sulfate decrease and pH increases as one moves further downstream from the AMD sources. This is a natural result of attenuation, dilution by uncontaminated water, and precipitation of iron-rich phases along the affected channels. Coprecipitation and adsorption of trace elements on these solid phases also play a role in contaminant attenuation, particularly for elements such as As and Pb (Olías et al. 2011; Valente et al. 2012a, 2013).

To illustrate the relationship between the contaminant concentrations at the generating source and the receiving river, a graphical representation was performed with data

**Table 2** Hydrochemical characterization of the receiving watercourses

Sub-basin									
Parameter	Trimpancho	Malagón	Cobica	Meca	Oraque	Olivargas	Odiel	Tinto	Guadiamar
pH	2.45	4.83	2.57	2.57	2.93	5.25	3.41	2.13	6.49
EC ( $\mu\text{S}/\text{cm}$ )	781	1087	498	746	302	171	382	771	187
TSD (mg/L)	500	695	310	475	193	110	244	493	120
SO <sub>4</sub> <sup>2-</sup> (mg/L)	1060	31	510	720	188	130	384	690	130
Fe (mg/L)	30.26	0.30	32.18	34.13	4.91	0.30	1.46	62.24	0.30
Cu (mg/L)	6.59	0.01	4.85	7.14	1.41	0.04	3.61	12.70	0.001
Pb (mg/L)	0.05	0.32	0.32	0.38	0.36	0.38	0.39	0.44	0.33
Cd (mg/L)	0.078	0.248	0.050	0.038	0.006	ND	0.025	0.047	0.278
Zn (mg/L)	4.53	ND	2.02	12.16	5.47	0.93	8.23	9.85	ND
Mn (mg/L)	9.54	0.03	1.51	6.55	0.08	0.80	4.75	4.64	0.07
Co (mg/L)	0.161	0.043	0.023	0.531	0.052	0.016	0.101	0.279	0.042
Ni (mg/L)	0.133	0.008	0.007	0.193	0.006	0.005	0.022	0.068	0.008
Mg (mg/L)	96.69	36.05	89.79	49.78	64.01	56.03	44.56	74.84	12.35
Ca (mg/L)	17.80	59.59	39.49	29.76	23.21	38.06	44.66	28.45	53.52
Al (mg/L)	0.50	0.50	0.35	0.51	0.45	0.48	0.40	0.54	0.78
As (mg/L)	ND	ND	0.001	0.007	0.001	ND	0.005	0.012	0.003
Sb (mg/L)	0.019	0.001	0.002	0.035	0.007	0.004	0.027	0.033	0.016

ND: below the detection limit (0.001  $\mu\text{g}/\text{L}$ )

from the Tinto river basin. Figure 2 presents the analysed parameters in the Tinto River as well as at each mine site. This river was selected because of the paradigmatic nature of the Tinto River, due to its high contamination levels. Figure 2 highlights the contribution of the Riotinto mine, which showed the highest values of sulfate, EC, TDS, Fe, Zn, Mn, Co, Ni, and Al, as well as contaminant contributions mostly from the Peña del Hierro, La Chaparrita, and La Ratera mines. In contrast, for the other mines located in the basin, the concentrations in the Tinto River were generally higher than in the discharged leachates.

Conversely, the pH of the river was slightly higher than the minimum observed in the basin ( $\text{pH}=2.13$ ), which corresponds to the Riotinto mine, and was lower than most of the other mine leachates. There are three reasons for this: one is that the Riotinto mining group is the largest AMD source in the IPB, and its contributions are more important than those of the other mines; two, the precipitation of iron in the river contributes acidity and lowers the pH; and three the large waste dumps of the Riotinto Mine produce leachate discharges for much longer than the smaller mine waste dumps.

In addition to this, in the Riotinto mine, various open pits and underground operations are connected by a complex system of galleries, especially by Tunnel 16. This transfers water from the Odiel watershed (from Corta Atalaya) to the Tinto watershed (Grande et al. 2010b). TDS, sulphate, and EC have similar trends, in accordance with the literature (Lyew and Seppard 2001; de la Torre et al. 2011; Grande et al. 2005, 2013; Valente et al. 2012b, 2013), because sulfate is a key component of the TDS and EC variations. This happens in the absence of chlorides, often responsible for significant EC increases elsewhere, which could mask the

dependency relationships between conductivity and sulfate, as can happen where AMD from fluvial origins enter into an estuarine environment (Grande et al. 2003a, b).

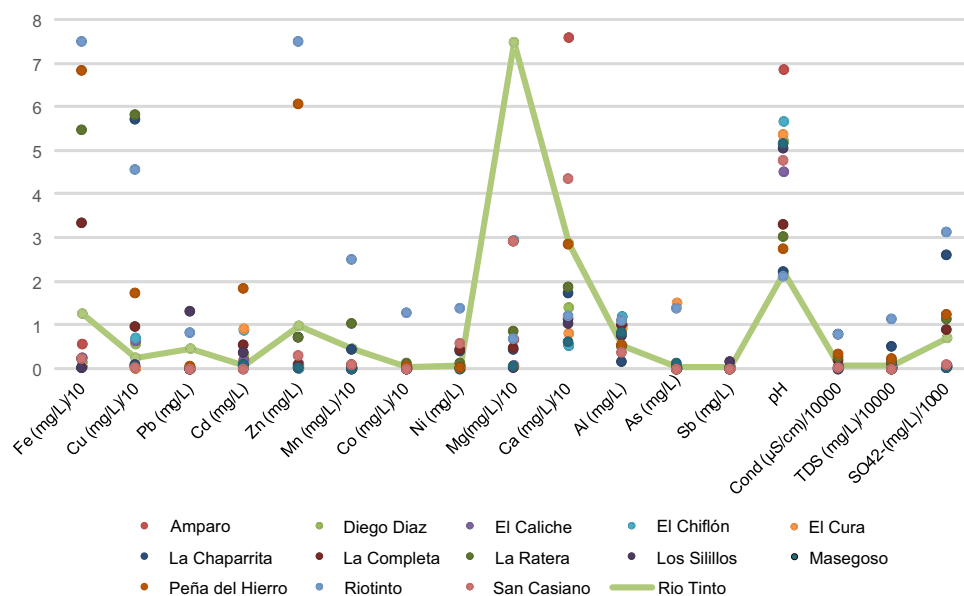
## Conclusions

The results of this study provide a high-level picture of the effects of AMD in the river network of the IPB. A novel point of this work was the hydrochemical characterization of the AMD-generating sources for an entire metallogenic province. For most of the leachates, the values are representative of an environment affected by AMD, with pH values between 2.01 and 7.75. In particular, the pH was lowest at the Riotinto Mine, where the concentrations of sulfate (3850 mg/L), conductivity (41,300  $\mu\text{S}/\text{cm}$ ), Zn (75.01 mg/L), Mn (28.74 mg/L), Cd (2.54 mg/L), and Co (12.91 mg/L) were the highest. The least affected leachates were generally found at the small mines.

Most of the main watercourses had pH values between 2.13 and 3.41, except for the less affected Malagón, Olivargas, and Guadamar rivers. There was a clear trend of decreasing metals, arsenic, and sulfate concentrations between the AMD sources and the rivers, while pH increases. These trends denote a decrease in water pollution as leachates flow from the discharge points due to dilution, precipitation of Fe oxyhydroxides and oxyhydroxysulfate in the affected channels, and coprecipitation with or adsorption onto the iron precipitates.

The duration of leachate discharges depends on the size of the waste dumps: the small ones remain dry most of the year, and leaching occurs only briefly after rain. Consequently, their contributions are irrelevant to the overall annual load,

**Fig. 2** Concentration of metals, arsenic and physical–chemical parameters in the Tinto River basin. The points represent mining leachates while the line describes the concentrations obtained in the river



despite the highly polluted nature of some of them. By contrast, the large dumps produce leachate discharges long after rainfall has ceased. The Riotinto mining group, which occupies the largest area in the watershed, has the greatest impact on the hydrochemistry of the Tinto River.

In conclusion, this approach proved to be useful for diagnosing the effects of AMD on the river network of an entire metallogenic province. Furthermore, the information obtained in this study will aid land management and the development of strategies oriented to the preservation and improvement of the river network quality within the framework of the European Union environmental regulations.

## References

- Carrasco I (2000) Riotinto: Cuna de la minería (Historia y minería de la Faja Pirítica Ibérica). *Bocamina* 5:10–49 (in Spanish)
- de la Torre ML, Sánchez-Rodas D, Grande JA, Gomez T (2010) Relationships between pH, colour and heavy metal concentrations in the Tinto and Odiel rivers. *Hydrol Res* 41(5):406–413
- de la Torre ML, Grande JA, Graiño J, Gómez T, Cerón JM (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
- Elbaz-Poulichet F, Braungardt C, Achterberg E, Morley N, Cossa D, Beckers J, Nomérage P, Cruzado A, Leblanc M (2001) Metal biogeochemistry in the Tinto–Odiel rivers (Southern Spain) and in the Gulf of Cádiz: a synthesis of results of TOROS project. *Cont Shelf Res* 21(18–19):1961–1973
- Flores Caballero M (1983) La rehabilitación Borbónica de las minas de Riotinto. Instituto de Estudios Onubenses, Padre Marchena, pp 1725–1810
- Grande JA, Borrego J, de la Torre ML, Sáinz A (2003a) Application of cluster analysis to the geochemistry zonation of the estuary waters in The Tinto and Odiel rivers. *Environ Geochem Health* 25:233–246
- Grande JA, Borrego J, Morales JA, de la Torre ML (2003b) A description of how metal pollution occurs in the Tinto–Odiel rivers (Huelva–Spain) through the application of cluster analysis. *Mar Pollut Bull* 46:475–480
- Grande JA, Beltrán R, Sáinz A, Santos JC, de la Torre ML, Borrego J (2005) 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, 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, de la Torre ML (2010b) 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* 176:395–401
- Grande JA, Santisteban M, de la Torre ML, Valente T, Pérez-Ostale E (2013) Characterisation of AMD pollution in the reservoirs of the Iberian pyrite belt. *Mine Water Environ* 32:321–330
- Grande JA, Valente T, de la Torre ML, Santisteban M, Cerón JC, Pérez-Ostale E (2014) Characterization of acid mine drainage sources in the Iberian pyrite belt: base methodology for quantifying affected areas and for environmental management. *Environ Earth Sci* 71:2729–2738
- Jiménez A, Aroba J, de la Torre ML, Andújar JM, Grande JA (2009) Model of behaviour of conductivity versus pH in acid mine drainage water, based on fuzzy logic and data mining techniques. *J Hydroinform* 11(2):147–153
- Leblanc M, Morales JA, Borrego J, Elbaz-Poulichet F (2000) 4500 years old mining pollution in southwestern Spain: long-term concerns for modern mining pollution. *Econ Geol* 95:655–662
- Leistel JM, Marcoux E, Thieblemont D, Quesada C, Sánchez A, Almodóvar G, Pascual S, Sáez R (1998) The volcanic hosted massive sulfide deposits of the Iberian pyrite belt. *Miner Depos* 33:2–30
- Loredo J, Pendás F (2005) Implicaciones de la Directiva Marco en la gestión de aguas de minas. In: López-Geta JA, Pulido Bosch A, Baquero Úbeda JC (eds) *Agua, minería y medio ambiente. Libro homenaje al profesor Fernández-Rubio*. IGME, Madrid, pp 535–544 (in Spanish)
- Lyw D, Sheppard J (2001) Use of conductivity to monitor the treatment of acid mine drainage by sulfate-reducing bacteria. *Water Res* 35(8):2081–2086
- Olías M, Nieto JM, Sarmiento AM, Canovas CR, Galvan L (2011) Water quality in the future Alcolea reservoir (Odiel River, SW Spain): a clear example of inappropriate management of water resources in Spain. *Water Resour Manage* 25(1):201–215
- Pérez-Ostale E, Grande JA, de la Torre ML, Valente T, Cerón JC, Santisteban M (2013) Inventory of mining and quantification of affected areas in the Iberian pyrite belt (SW Spain). Methodological contribution to environmental management. *Proc Int Multidiscip Sci Geoconf* 1:613–621
- Sáinz A (1999) Estudio de la Contaminación Química de Origen Minero en El Río Odiel. PhD Thesis, Univ of Huelva (in Spanish)
- Sáinz A, Grande JA, de la Torre ML, López N (2000) Análisis de la contaminación por AMD en la cuenca del río Odiel. *Residuos* 57:91–99 (in Spanish)
- 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 Manage* 64:345–353
- Sáinz A, Grande JA, de la Torre ML (2004) Characterisation of heavy metal discharge into the Ria of Huelva. *Environ Int* 20:557–566
- Sánchez-España J, López-Pamo E, Santofimia E, Aduvire O, Reyes J, Martín JA (2006) The impact of acid mine drainage on the water quality of the Odiel river (Huelva, Spain): evolution of precipitate mineralogy and aqueous geochemistry along the Concepcion-Tintillo segment. *Water Air Soil Pollut* 173:121–149
- Sarmiento AM (2007) Estudio de la contaminación por drenajes ácidos de mina de las aguas superficiales en la cuenca del río Odiel (SO España). PhD Thesis, Univ de Huelva, ISBN: 978-84-16061-03-7 (in Spanish)
- Valente T, Antunes M, Sequeira Braga MA, Prudêncio MI, Marques R, Pamplona J (2012a) Mineralogical attenuation for metallic remediation in a passive system for mine water treatment. *Environ Earth Sci* 66:39–54
- Valente T, Ferreira MJ, Grande JA, de la Torre ML, Borrego J (2012b) pH, electrical conductivity and sulfate as base parameters to estimate the concentrations of metals and arsenic in AMD using a fuzzy inference system. *J Geochem Explor* 124:22–28
- Valente T, Grande JA, de la Torre ML, Santisteban M, Cerón JC (2013) Mineralogy and environmental relevance of AMD-precipitates from the Tharsis mines, Iberian Pyrite Belt (SW, Spain). *Appl Geochem* 39:11–25