

Relationships between pH, colour and heavy metal concentrations in the Tinto and Odiel rivers (southwest Spain)

M. L. de la Torre, D. Sánchez-Rodas, J. A. Grande and T. Gomez

ABSTRACT

The relationships between pH, colour, Fe, Mn, Cu, Zn, Cd and sulphates in surface water samples collected from the Tinto and Odiel Rivers (southwest Spain) have been studied. These rivers are adversely affected by the inputs of acid and heavy metals due to Acid Mine Drainage (AMD). Samples were collected from both rivers on a monthly sampling basis from 1995 to 2001. The analytical results showed that pH (mean pH 3.1) in the water samples of the Odiel River presented a greater correlation with heavy metals, colour and sulphates than in the Tinto River (mean pH 2.5). The tidal effect at the sampling point at the Odiel River appears to cause a greater variation of the pH values (2.5–4.4), resulting in the precipitation of iron hydroxide and the co-precipitation of other metals when the pH increased. This phenomenon was not observed in the samples collected from the more acidic Tinto River (pH 2.1–3.2). A similar relationship was observed for the heavy metals and the colour of the surface water of both rivers.

Key words | acid mine drainage (AMD), colour, heavy metals, pH, Rio Odiel, Rio Tinto

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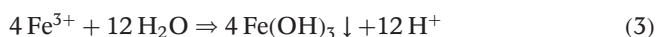
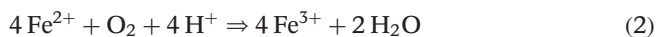
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INTRODUCTION

The Tinto and Odiel Rivers (southwest Spain) are affected by Acid Mine Drainage (AMD) that originates from the oxidation and lixiviation of sulphurous rocks containing metals (pyrites) that are exposed to oxygen and water. AMD is characterized by high acidity and an elevated concentration of heavy metals and sulphates (Lyew & Sheppard 2001). The chemical reactions that describe the dissolution of pyrite and the resulting production of AMD are the following:



There are two mechanisms involved in the chemical oxidation of pyrite: a direct mechanism using the

molecular oxygen as the oxidizing agent (Equations (1) and (2)), and an indirect or propagation mechanism where the ferric cation is the oxidizing agent (Equation (4)). Both mechanisms take place at the same time but at different kinetic rates, depending on the pH value. This process also depends on the type, abundance and distribution of sulphides, minerals with neutralizing capacity, oxygen concentration, humidity, temperature and pyritic exposed surface area (Rose & Cravota 1998; Dogan 1999). Under natural conditions, this chemical process is very slow. The oxidation of pyrite can however be accelerated by the presence of chemolithotrophic bacteria such as *Thiobacillus ferrooxidans* at low pH values (Kim & Chon 2001), capable of speeding up the oxidation of Fe^{2+} to Fe^{3+} (Equation (2)) by 5–6 orders of magnitude. The importance of the bioleaching of sulphide minerals by this type of bacteria has been reviewed (Nemeti *et al.* 1998).

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The heavy metal pollution of surface water caused by AMD is difficult to remediate. It is important to have an understanding of the physical and chemical processes governing pollutant releases over time (Younger 1997). The presence of some metallic ions in solution, such as Fe and Mn, contribute to the colour of the water bodies. Although colour has been used to estimate the oxidized Fe content in mine waste rocks (Shum & Lavkulich 1999), to our knowledge the literature does not consider a possible relationship between colour, heavy metal content and pH for waters affected by AMD.

The Spanish Ministry for the Environment designed a control network in order to assess the quality of the continental waters, the so-called ICA network (*Red Integrada de la Calidad de las Aguas*, Integrated Network of the Water Quality), introduced in 1993. The ICA comprises previous existing networks in Spain with surface water data from over 1,000 sampling points. Among others, the ICA includes the COCA network (*Red de Control Oficial de la Calidad de las Aguas*, Official Network of Water Quality) which has been systematically regulating the quality of surface waters since 1962, measuring a total of 40 analytes.

The objective of this work is to establish relationships between pH, colour and the concentration of sulphates and several heavy metals (Fe, Cu, Zn, Cd and Mn) in two surface water bodies affected by AMD. The COCA network provided the data from a sampling location in each of the Tinto and Odiel rivers.

The Tinto and Odiel rivers are located in southwest Spain (Figure 1) within the Iberian Pyrite Belt, a volcanogenic massive sulphide deposit (ca. 200 km long and 40–60 km wide) that constitutes one of the most important metallurgic regions in the world. The original sulphide mineral resources have been estimated at 750 million tons (Sáinz *et al.* 2002).

Both rivers have high concentrations of heavy metals and extremely low pH values of less than 3 (Borrego 1992; Braungardt *et al.* 1998; Elbaz-Poulichet *et al.* 1999; Davis *et al.* 2000; Grande *et al.* 2000, 2003a,b; Sainz *et al.* 2002, 2003a,b). Their contribution to the contamination of the estuary is estimated at ca. 1.2×10^6 tons/year of sulphates and 2.0×10^4 tons/year of heavy metals. The potential contamination from both rivers is of major importance.

If a rainy year is considered, in a single week their waters can transport as much heavy metals as was transported during the mining accident of Aznalcollar in 1998 which affected the Guadiamar River (Elbaz-Poulichet *et al.* 1999; Sáinz *et al.* 2000).

MATERIALS AND METHODOLOGY

Sampling methodology

Samples were collected monthly from January 1995 to December 2001. Water samples were collected using 100 mL polyvinyl chloride containers from two sampling points. One sampling point was located at the Tinto River (roman bridge at the village of Niebla) and the other at the Odiel River (village of Gibraleón) (Figure 1). pH was measured *in situ* with a portable pH-meter. Two samples were taken at each sampling point; one was preserved by acidification with HNO₃ to pH <2 and stored at 4°C in order to maintain metals in solution during transport to the laboratory. A second sample was collected and not acidified, in order to measure the sulphate concentration.

Reagents and apparatus

All reagents were of analytical grade or Suprapure quality (Merck, Darmstadt, Germany). Stock standard solutions were Merck Certified AA standards. Aqueous solutions were prepared with Milli-Q water (Millipore, Bedford, MA). Heavy metals determination in the water samples were performed using an Atomic Absorption Spectrophotometer model AAnalyst 700 (Perkin Elmer, Norwalk, US) equipped with flame and graphite furnace atomizers. Sample introduction was carried out using the Perkin-Elmer Autosampler model AS800. Hollow cathode lamps used as radiation sources were Perkin-Elmer Lumina.

A DX-120 Ion Chromatograph from Dionex (Sunnyvale, CA) equipped with an analytical column (IonPac AS9-HC, 250 × 4 mm), a conductivity detector, an Autosampler model AS40 and a self-regenerating suppresser column (ASRS-ULTRA) was used for anion determination. For pH measurements a portable Crison pH-meter 507 was employed. Water samples were filtered with nylon 0.45 μm filters Millex SLCR 013 (Millipore).

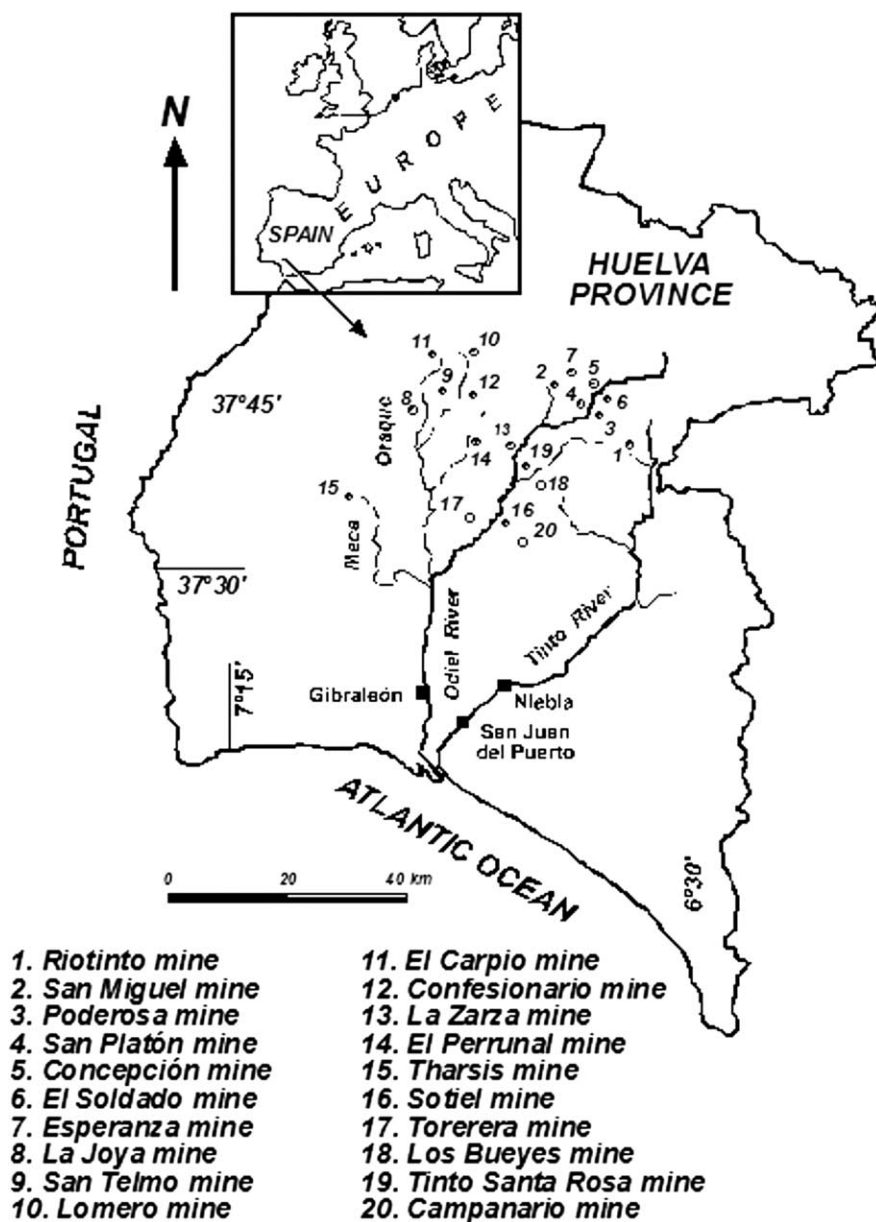


Figure 1 | Location map.

Analytical procedures

Fe, Cu, Mn, Zn and Cd concentrations in water samples were determined by Atomic Absorption Spectrometry. The accuracy of the analytical procedures for total metal determinations was checked with CRM 609 (trace elements in groundwater) from BCR. Replicated analyses showed results comparable with the certified values. Sulphate was

determined by ion chromatography with chemical suppression of Eluant conductivity (Standard Methods, 4100). The accuracy of the analytical procedures for sulphate determination was checked with CRM 408 (major compounds in simulated rainwater) and CRM 609 (trace elements in groundwater) from BCR. Colour was measured as mg Pt/L units (Pt. U.) by comparison with Pt-Co solutions (Standard Methods, 2120B) after sample filtration.

Table 1 | Statistical results of the parameters analyzed at the Tinto River sampling point (sampling period: monthly from January 1995 to December 2000; LD: limit of detection where Mn: 0.01; Cu: 0.05; Zn: 0.01; Cd: 0.001; Fe: 0.01)

Summary	Colour (U. Pt)	pH	SO ₄ ²⁻ (mg/l)	Mn (mg/l)	Fe (mg/l)	Cu (mg/l)	Zn (mg/l)	Cd (mg/l)
Average	3,991.3	2.5	2,705.3	12.9	489.3	32.7	77.5	0.24
Variance	3.1 × 10 ⁷	0.05	5.4 × 10 ⁶	190.2	45,1984	1,769.5	7,335.5	0.1
Minimum	5	2.1	178	< LD	5.2	< LD	< LD	< LD
Maximum	33,025	3.2	9,999	84.7	4,668.4	296.3	443.4	1.3

Statistical analysis

The statistical analysis compared mean values and variances of the different parameters obtained from both sampling locations. A multivariable study was conducted considering the correlation matrixes (Bisquerra 1989) by means of the statistical package Statgraphics Plus for Windows 5.1. In these matrices, each individual square contains the ordinal coefficient of Spearman which varies between 1 and -1 and the significance level of estimated correlation for each pair of variables (Bisquerra 1989). A correlation among variables is considered when the Spearman coefficient value is greater than 0.5.

RESULTS

The statistical results obtained with univariate analysis are summarized in Tables 1 and 2 for the Tinto and Odiel Rivers, respectively. Surface water in the Tinto River is more acidic (mean pH 2.5) than the Odiel River (mean pH 3.2), and the variance is twice as high at the Odiel River sampling location than at the Tinto River. Colour reaches an elevated mean value of 3,991 Pt. U. for the Tinto River whereas for the Odiel River the colour mean value is only 83 Pt. U. The variance in the colour is considerably higher for the Tinto River. The average concentrations of heavy metals in the Tinto River are in all cases always higher than in the

Odiel River. The concentration of Fe is most noticeable, with concentrations about 30 times higher than in the Odiel River. The average concentrations of Cu, Zn and Cd were about 3–5 times higher than in the Odiel River. Similar average values were only found for Mn. Tables 1 and 2 also include the sulphate ion, as its concentration is related to the presence of heavy metals. The results obtained show that the average sulphate concentration in the Tinto River is twice as high as in the Odiel River.

Table 3 lists the results of the correlation matrix of the variables in the Tinto River, which indicated that there is a moderate and negative correlation between pH, heavy metals, sulphates and colour. On the other hand, the results obtained for the Odiel River (Table 4) concerning the pH show a different pattern. In this case, there is a high and negative correlation between pH, heavy metals, colour and sulphates. Colour follows a similar pattern in the samples collected from both rivers, with a high and positive correlation considering heavy metals and sulphate. The correlation of colour with pH is higher for the Odiel River than for the Tinto River.

Figures 2 and 3 shows the scatterplots corresponding to previous variables for the Tinto and Odiel rivers, respectively. The relation among paired variables described in the correlation matrices is highlighted. It can be observed that, for some variables, the relation between them is not linear but quadratic. This is the case for pH and colour for the

Table 2 | Statistical results of the parameters analyzed at the Odiel River sampling point (sampling period: monthly from January 1995 to December 2000; LD as for Table 1)

Summary	Colour (U. Pt)	pH	SO ₄ ²⁻ (mg/l)	Mn (mg/l)	Fe (mg/l)	Cu (mg/l)	Zn (mg/l)	Cd (mg/l)
Average	83.8	3.17	1,117.2	12.6	15.5	5.9	21.6	0.1
Variance	16,126.1	0.1	496,586	79.5	597.6	7.1	302.5	0.1
Minimum	5	2.5	70.3	< LD	< LD	< LD	< LD	< LD
Maximum	660	4.4	3,040	38.4	171	12.7	68.7	0.2

Table 3 | Correlation matrix obtained for the Tinto River data. In each cell is indicated, first, the correlation coefficient between each pair of variables and second, the statistical significance of the estimated correlations (values less than 0.05 indicate a level of confidence of 95)

	Colour	pH	SO ₄ ²⁻	Mn	Fe	Cu	Zn
pH	-0.3098 (62)						
SO ₄ ²⁻	0.0143 0.6941 (59)	-0.4077 (67)					
Mn	0.0000 0.8559 (60)	0.0006 -0.3015 (65)	0.9334 (63)				
Fe	0.0000 0.9321 (61)	0.0146 -0.2989 (66)	0.0000 0.8794 (64)	0.9320 (65)			
Cu	0.0000 0.8992 (57)	0.0108 -0.3297 (59)	0.0000 0.8969 (57)	0.0000 0.9404 (57)	0.9708 (57)		
Zn	0.0000 0.8495 (54)	0.0046 -0.3703 (57)	0.0000 0.9334 (55)	0.0000 0.9691 (54)	0.0000 0.9249 (54)	0.9068 (55)	
Cd	0.0000 0.8667 (51)	0.0046 -0.3830 (53)	0.0000 0.9198 (50)	0.0000 0.9448 (51)	0.0000 0.8893 (51)	0.0000 0.8864 (51)	0.9191 (52)
	0.0000	0.0046	0.0000	0.0000	0.0000	0.0000	0.0000

Tinto River in Figure 2, corresponding to the lower correlation previously described. The points of this graph are closer and can be adjusted to a curve. For the Odiel River (Figure 3), the points of the graph can be better fitted to a curve. Outliers can be found for both figures, something that is characteristic in waters affected by AMD. It is worth mentioning that, for both rivers for some paired variables (sulphates and one metal, or two metals), the relation is linear.

DISCUSSION

The pH values detected in surface water samples from Tinto River (pH 2.1–3.2, average 2.5) are similar to the pH values reported by other authors (pH ~2.5, Elbaz-Poulichet *et al.* 1999; Canovas *et al.* 2007), suggesting that pH for both rivers has remained fairly constant throughout the year. As for the Odiel River, our data indicated that the pH ranged from

2.5–4.4 with an average of 3.2. This result is somewhat higher than that reported by Elbaz-Poulichet *et al.* (pH ~ 2.8), and is likely due to the tidal effect on surface water that can be noticed at the Gibraleón sampling point (Grande *et al.* 2003b). The influence of the seawater is highlighted by the fact that the variance of the pH at the sampling point of the Odiel River is double that for the Tinto River (0.13 compared to 0.06). This explains the wider range of pH values found for the Odiel River (Table 2). The greater pH stability of the Tinto river system is also a consequence of the buffer reaction developed between the ferric iron and some cationic complex such as Fe(OH)₂⁺ (Elbaz-Poulichet & Dupuy 1999).

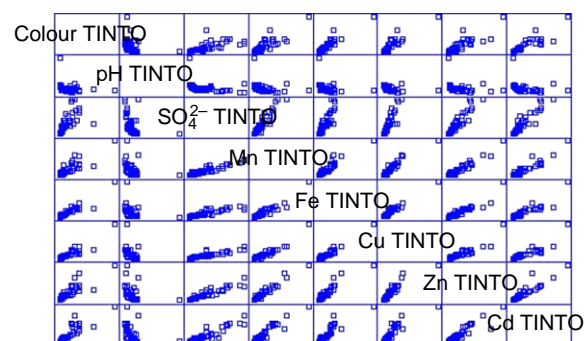
The pH is a critical variable to study the diminution of heavy metals concentration in solution due to precipitation. As indicated in Table 3, there is a moderate correlation between the pH of the water samples of the Tinto River and all measured heavy metals (Spearman -0.50 to -0.66).

Table 4 | Correlation matrix for the Odiel River data. In each cell is indicated, first, the correlation coefficient between each pair of variables and second, the statistical significance of the estimated correlations (values less than 0.05 indicate a level of confidence of 95)

	Colour	pH	SO ₄ ²⁻	Mn	Fe	Cu	Zn
pH	-0.4657 (61) 0.002						
SO ₄ ²⁻	0.5907 (60) 0.0000	-0.7154 (68)					
Mn	0.5126 (58) 0.0000	-0.6413 (64)	0.8915 (64)				
Fe	0.8658 (58) 0.0000	-0.4305 (64)	0.5771 (64)	0.4666 (64)			
Cu	0.5959 (57) 0.0000	-0.7625 (60)	0.8526 (60)	0.8221 (57)	0.5363 (57)		
Zn	0.5818 (53) 0.0000	-0.6656 (56)	0.8538 (56)	0.9591 (53)	0.6199 (53)	0.8063 (56)	
Cd	0.5802 (50) 0.0000	-0.7353 (52)	0.8999 (51)	0.9567 (50)	0.5590 (50)	0.8431 (51)	0.9316 (51)

This can be explained by the fact that as the pH values measured 2.1–3.2, all the considered metals remain in solution as their precipitation as hydroxides occurs at higher pH values (Fe: 3.5–4.5, Cu: 6.5–7.5; Zn: 8.0–9.5; Mn: 8.5–9.5) (Singh & Rawat 1985). This also explains the accumulation of points in the scatterplot that considers pH and metals (Figure 2). A different trend is observed at the Odiel River, with a high and negative correlation between pH with all the measured heavy metals (Spearman: -0.64 to -0.86). In this case, the pH reaches values up to 4.4 where the precipitation of iron can occur. The tidal effect at the Gibraleón sampling location results in a maximum pH of 4.4 due to the mixing with the basic seawater. It is also known that an increase in the pH and the consequent iron precipitation produces the co-precipitation of other metals (Willer & Hunter 1977) even before their precipitation pH values are reached; this explains the non-linear relation found for colour and pH with sulphates and metals.

The colour of the river water is related mainly to the Fe and Mn content. This is corroborated by both rivers. The relationship between colour and Fe content is also confirmed, considering that the colour of the Tinto River is about 48 times more intense than the Odiel River (3,991 to 83.8 Pt. U.) and that the concentration of Fe in the Tinto River is about 32 times greater at the Tinto River than at the

**Figure 2** | Scatterplot corresponding to variables for the Tinto river.

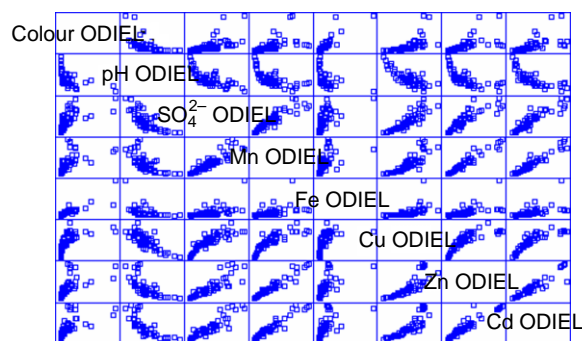


Figure 3 | Scatterplot corresponding to variables for the Tinto river.

Odiel River (489.3 to 15.5 mg/l). As expected, colour also correlates positively with Mn at both the Tinto and Odiel Rivers (0.83 and 0.75, respectively). The not so high correlation found between colour and pH at the Tinto River (Spearman: -0.57) (Table 3) is explained by the fact that Fe and Mn remain in solution under the stable acidic conditions of this river. However, at the Odiel River, increments in the pH produce a subsequent diminution of Fe and Mn concentrations, thus explaining the negative and more significant correlation (Spearman: -0.73) between colour and pH (Table 4). The high and positive correlation of the heavy metals and sulphate for both rivers is explained as metals can form complexes with this one anion as MSO_4^+ and $\text{M}(\text{SO}_4)^{2-}$ (Elbaz-Poulichet & Dupuy 1999).

CONCLUSIONS

The surface water sampling results from both rivers indicates a high correlation between pH and heavy metals only for the Odiel River, as a tidal effect at this sampling location results in the precipitation of Fe and co-precipitation of other metals. The more acidic Tinto surface water samples appeared to result in metals remaining in solution.

Colour showed a similar trend in both rivers when heavy metals are considered, presenting a high correlation with all the studied heavy metals (especially Fe and Mn). When the pH is considered, colour at the Odiel decreases as the pH increases due to the precipitation of Fe and Mn.

The results of our work correspond to a local study, but can be considered as a first approximation for the development of methods based on colour and pH as suitable parameters for characterizing water bodies affected by AMD.

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REFERENCES

- Bisquerra, R. 1989 *Introducción Conceptual al Análisis Multivariable*. PPU, SA, Barcelona.
- Borrego, J. 1992 Sedimentología del estuario del río Odiel, Huelva. SO España. PhD Thesis. University of Sevilla.
- Braungardt, C. B., Achterberg, E. P. & Nimmo, M. 1998 Behaviour of dissolved trace metals in the rio Tinto/rio Odiel Estuarine System. In: Morales, J. A. & Borrego, J. (eds) *European Land-Ocean Interaction Studies*, Second Annual Scientific Conference: Abstracts 51.
- Canovas, C. R., Olías, M., Nieto, J. M., Sarmiento, A. M. & Cerón, J. C. 2007 Hydrogeochemical characteristics of the Tinto and Odiel rivers (SW Spain). Factors controlling metal contents. *Sci. Total Environ.* **373**, 363–382.
- Davis, R. A. Jr., Welty, A. T., Borrego, J., Morales, J. A., Pendón, J. G. & Ryan, J. G. 2000 Rio Tinto estuary (Spain): 5000 years of pollution. *Environ. Geol.* **39**, 1107–1116.
- Dogan, P. A. 1999 Characterization of mine waste for prediction of acid mine drainage. In: Azcue, J. M. (ed.) *Environmental Impacts of Mining Activities*. Springer, Berlin, pp. 19–38.
- Elbaz-Poulichet, T. & Dupuy, C. 1999 Behavior of rare earth elements at the freshwater-seawater interface of two acid mine rivers: the Tinto and Odiel (Andalucía, Spain). *Appl. Geochem.* **14**, 1063–1072.
- Elbaz-Poulichet, F., Morley, N. H., Cruzado, A., Velasquez, Z., Achterberg, E. P. & Braungardt, C. B. 1999 Trace metal and nutrient distribution in an extremely low pH (2.5) river-estuarine system, the Ria of Huelva (southwest Spain). *Sci. Total Environ.* **227**, 75–83.
- Grande, J. A., Borrego, J. & Morales, J. A. 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, J. A., Borrego, J., de la Torre, M. L. & Sáinz, A. 2003a 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, J. A., Borrego, J., Morales, J. A. & de la Torre, M. L. 2003b A description of how metal pollution occurs in the Tinto-Odiel rias (Huelva-Spain) through the application of cluster analysis. *Mar. Pollut. Bull.* **46**(4), 475–480.
- Kim, J. & Chon, H. 2001 Pollution of a water course impacted by acid mine drainage in the Imgok creek of the Gangreung coal field, Korea. *Appl. Geochem.* **16**, 1387–1396.
- Lewy, D. & Sheppard, J. 2001 Use of conductivity to monitor the treatment of acid mine drainage by sulphate-reducing bacteria. *Water Res.* **35**(8), 2081–2086.

- Nemeti, M., Harrison, S. T. L., Hansford, G. S. & Webb, C. 1998 Biological oxidation of ferrous sulphate by *Thiobacillus ferrooxidans*: a review on the kinetics aspects. *Biochem. Eng. J.* **1**, 171–190.
- Rose, A. W. & Cravota, C. A. 1998 Geochemistry of a coal mine drainage. In: Brady, K. B. C., Smith, M. W. & Schueck, J. (eds) *Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania*. The Pennsylvania Department of Environmental Protection, Pennsylvania, pp. 1–22.
- Sáinz, A., Grande, J. A., de la Torre, M. L. & López, N. 2000 Caracterización de procesos de AMD y ARD en la cuenca del río Odiel. *Ingeopres* **88**, 52–60.
- Sáinz, A., Grande, J. A., de la Torre, M. L. & 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, J. A. & de la Torre, M. L. 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, J. A. & de la Torre, M. L. 2003b Odiel river, acid mine drainage and current characterisation by means of univariate analysis. *Environ. Int.* **29**, 51–59.
- Shum, M. & Lavkulich, L. L. 1999 Use of sample color to estimate oxidized Fe content in mine waste rock. *Environ. Geol.* **37**, 281–289.
- Singh, G. & Rawat, N. S. 1985 Removal of trace elements from acid mine drainage. *Int. J. Mine Water* **2**, 817–827.
- Willer, W. G. & Hunter, J. V. 1977 Aquatic transport of heavy metals in the urban environment. *Water Resour.* **13**, 721–734.
- Younger, P. L. 1997 The longevity of minewater pollution: a basis for decision-making. *Sci. Total Environ.* **194–195**, 457–466.

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