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Characterization of main AMD inputs to the Odiel River upper reach (SW Spain)

Julia Riera[a,1], Carlos R. Cánovas[a], Manuel Olías[a]

[a]*Department of Earth Sciences, University of Huelva, Campus El Carmen s/n, 21071 Huelva, Spain*

Abstract

The Iberian Pyrite Belt (IPB) is rich in sulfide deposits which have been intensively exploited, generating a huge problem of contamination of the Odiel River by acid mine drainage (AMD). At its source is a clean river, but along a 7 km-long reach receives five discharges of acid mine waters: Concepción, San Platón, Esperanza, Poderosa and the Agrio River, which drains the AMD contaminated water from the Río Tinto mines. The flows and hydrogeochemical characteristics of these AMD sources have been studied. The Agrio River is the main contributor of acidity, sulfate and metals to the Odiel River due to its high flows and pollutant concentrations. San Platón and Poderosa mines have high sulfate and metal concentrations although both sources are characterized by low or moderate flows while Concepción has the lowest concentrations but higher flows. The composition of AMD sources seem to be controlled by the mineralogy of the deposits and by geochemical processes. Strong seasonal variations are observed for some AMD sources while others are more constant throughout the year.

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Keywords: Iberian Pyrite Belt (IPB); sulphides; water pollution, AMD, metals

1. Introduction

The Odiel River basin (SW Spain) drains mines belonging to the Iberian Pyrite Belt (IPB), which is well known for hosting one of the biggest massive sulfide regions worldwide.

This mineral richness has led to intense mining activities along the basin generating a huge amount of wastes. The oxidation of sulfides contained in these wastes releases acidity, sulfate and metals, a water known as acid mine drainage (AMD), which is one of the main causes of water quality deterioration in the world. In the case of the Odiel basin, around 427 km of water courses are affected by AMD[1]. Odiel headwaters show a good quality status,

* Corresponding author. Tel.: +34-959-2195921; fax: +34-959-219440.
E-mail address: Julia.riera@dgyp.uhu.es

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however the confluence of the first mining discharges (i.e. Mina Concepción, San Platón, Esperanza and Poderosa; Fig. 1) cause the progressive deterioration of the water quality. This worsening becomes irreversible by the confluence of the Agrio River, which collects highly acidic and metal-rich discharges from the Río Tinto mines[2]. A geochemical characterization of these sources is needed to implement cost-effective treatment systems[3], especially considering the long term variations. Thus, the main goal of this study is to characterize geochemically the AMD sources causing the water quality deterioration in the Odiel upper reach.

2. Methodology

Geochemical data from the first AMD discharges flowing into a reach of the Odiel (Fig. 1) were obtained from several samplings performed between 2009 and 2015. Analytical results obtained by[1] since 2002 to 2006 were also used. The highest number of observations correspond to the Agrio River (n=25) while the lowest were obtained from San Platón mine (n=7). During all samplings the same methodology was followed; a sample was collected in each AMD source, filtered (through 0.2 µm), acidified to pH <2 and refrigerated until analysis by ICP-AES for main elements and ICP-MS for trace elements. Temperature, pH, electrical conductivity and oxidation-reduction potential (ORP) was measured in situ using a CRISON MM40+. Net acidity[4] was also calculated.

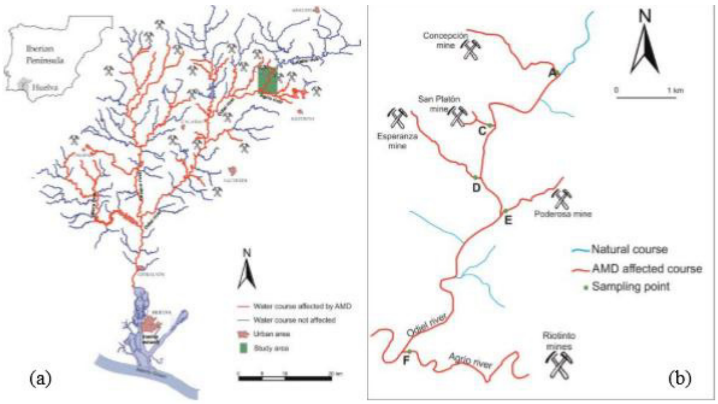

Fig. 1. (a) Location map of the Odiel basin; (b) study reach indicating all AMD sources sampled.

3. Results and discussion

Figure 2 shows the variation of some measured variables. All AMD sources had pH values ranging generally from 2 to 3. However, significant differences can be observed in the net acidity of each source; the highest values were observed for the Agrio River with average values of 4,400 mg/L of CaCO3, although values up to 20,000 mg/L can be reached during the dry season. The lowest values of net acidity were observed in Concepción with average values of 1,160 mg/L of $CaCO_3$ (Fig. 2). The highest flows were observed for the Agrio River, although a high variability is observed linked to the hydrological regime. Except Concepción (up to 20 L/s), the rest of discharges showed values below 10 L/s. A similar pattern is observed for sulfate and metals; it can be noted that the highest sulfate and most metal concentrations are recorded in the Agrio River (averages in ppm; 10,232 SO4, 785 Al, 82 Cu, 115 Mn and 176 Zn), which collects AMDs from Río Tinto. However, the highest Fe concentrations are reached in San Platón (1,506 ppm) although its discharge is of less significance (0.1-2.3 L/s). On the other hand, high concentrations of Cu were observed in Poderosa (Fig. 2) which may be related to the abundance of chalcopyrite, covellite and chalcocite5. High Cu concentrations were also observed in San Platón where higher Cu grades (up to 6.8%) than in Concepción (0.5-1.0%) and Esperanza (1-2%) are reported[5]. Concepción is the AMD source with the lowest level of sulfate and metals, however, it constitutes the second highest flow (generally 2-20 L/s). In relation to other AMD sources, Esperanza (1-3 L/s) has a moderate content of sulfate and metals (averages in ppm; 1857 SO_4, 75 Al, 18 Cu, 17 Mn and 142 Zn). A treatment plant to remediate acidic leachates of this mine started working in December 2014. Although downstream of the plant the effluent joins some AMD discharges from spoil heaps, a significant improvement of the water quality has been reached as commented below. Concerning seasonal variations, it can be noted that the lower concentrations are recorded during the rainy season when dilution processes by freshwater are prevalent. This pattern is especially significant in the Agrio River, which exhibits a high variability due to mixing processes with runoff. The low variability observed in San Platón is caused by less mixing with freshwaters. On the other hand, the highest values of sulfate and metal concentrations were observed generally during the dry season (May to September).

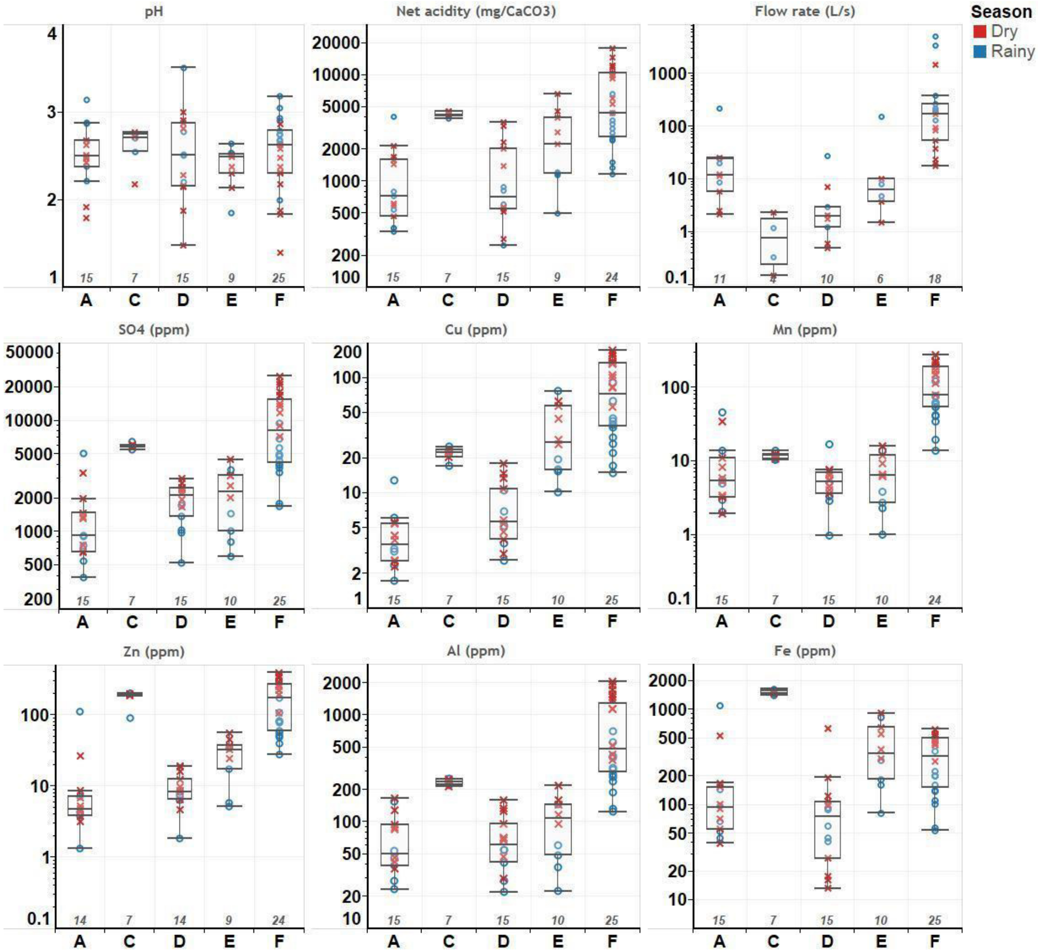

Fig. 2. Box and whisker plots of pH, net acidity, flow, and the concentration of sulfate and some metals in the AMD sources (A: Concepcion, C: San Platón, D: Esperanza, E: Poderosa and F: Agrio River). Base values indicate the number of samples of each discharge.

Geochemical processes can also modify the composition of AMD sources. Figure 3 represents the relation between Fe and base metals (i.e. Cu, Zn, Mn, Co, Cd and Ni) in the AMD sources and shows that two different groups can be differentiated. On the one hand, samples from Concepción, San Platón and Poderosa are aligned over a 5:1 ratio. On the other hand, samples from Agrio River are aligned with a 1:1 ratio. The Fe depletion observed in the Agrio River is caused by the precipitation of Fe minerals from its source to the sampling point at the confluence with the Odiel River. Samples from Esperanza follow a strikingly different distribution; a group of samples are close to the line 5:1 as the rest of sources, but another group are aligned over the 1:1 line (Fig. 3). This latter group corresponds to samples collected in 2015, when the treatment plant was working and thus, the Fe concentration in the effluent decreased in relation to base metals, with a more conservative behavior.

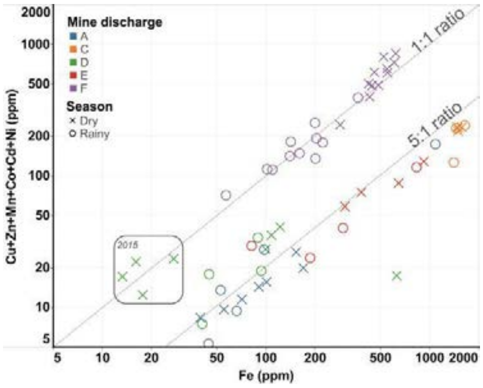

Fig. 3. Relationship between base metal and Fe concentrations for the AMD sources. Dotted lines represent ratio 1:1 and 5:1 (A: Concepcion, C: San Platón, D: Esperanza, E: Poderosa and F: Agrio River)

4. Conclusions

This study characterizes geochemically the AMD sources causing the water quality deterioration in the Odiel upper reach. The Agrio River is the main contributor of acidity, sulfate and metals to the Odiel River due to the high flows and concentrations observed. San Platón and Poderosa showed high sulfate and metal concentrations although both sources are characterized by low or moderate flows. On the other hand, Concepción showed the lowest concentrations but higher flows than the latter. The level of acidity and metals in AMD sources is dependent on the hydrological regime; during the dry season the highest concentration are observed and during the rainy period dilution processes causes a decrease in concentration. The AMD composition may be controlled by the mineralogy of the deposits and by geochemical processes. The Cu grade of sulfides seems to control Cu concentration in AMD sources. The precipitation of Fe also causes changes in the geochemical signature; waters from Agrio River are depleted in Fe in relation to base metals compared to the other sources. A similar case is observed in Esperanza waters from 2015, after the implementation of a treatment plant.

Acknowledgements

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