Effect of different sources and local conditions in the post-mining contamination by acid mine drainage: three case studies in Iberian Peninsula (SW Europe)

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Abstract

The Iberian Peninsula, comprising Portugal and Spain (SW Europe), has a long tradition of exploiting metals in different metallogenic provinces. The present study shows three cases of mining contamination in different regions of the Peninsula associated with distinctive acid mine drainage sources. Hydrochemical and mineralogical characterizations were performed for the three case studies. The results revealed the influence of ore deposit type, paragenetic, and climate diversity on hydrochemistry. Although different climate conditions and acid mine drainage sources exist, the relationships between physical-chemical indicators are similar for the distinctive sites. However, the magnitude of contamination is different, being highest in the Sa o Domingos mine (Iberian Pyrite Belt). The effect of natural attenuation is also verified, especially by dilution and precipitation. Seasonal variation is more pronounced in the rainiest region under study (Valdarcas mine).

Keywords: Valdarcas, são domingos, campanario, paragenesis, climate control

Introduction

Portugal and Spain have a long-lasting mining tradition, dating from pre-roman times. Noble metals, like gold and silver, and base metals, such as tin, copper, and tungsten, are among the essential resources exploited over centuries. Consequently, signs of degradation are associated with abandoned mining works crossing several regions in SW Europe, like the Iberian Pyrite Belt (IPB). Mine waters are usually the focus of environmental problems, with no borders on river contamination and habitat destruction (Lottermoser, 2010). Different types of ore deposits occur in the main metallogenetic provinces, with various amounts and types of sulfides. Consequently, acid mine drainage (AMD) associated with the evolution of sulfide-rich wastes is a common challenge in the environmental remediation of old mine sites. The region is also characterized by a high diversity of climate conditions that can control the geochemical evolution of sulfide wastes. The Atlantic's influence on climate is more intense in the northwest of the Peninsula, resulting in the rainiest conditions. On the other hand, the southwest, with a higher Mediterranean influence, is characterized by high temperatures and low precipitation. Prolonged periods of drought and scarcity are typical and increasingly frequent in this region of the Peninsula (Gomes et al., 2018). Also, there are important differences regarding geology and mining activity. The IPB, in the southwest, is one of the largest metallogenic provinces in the world, with massive sulfide deposits, with pyrite, sphalerite, chalcopyrite, galena, arsenopyrite, and sulfosalts (Inverno et al., 2015). In the north, there are numerous abandoned sites, including tin, gold, and tungsten mines in different types of ore deposits (e.g., pegmatites, hydrothermal, skarns) with variable amounts of sulfides (Valente and Gomes, 2009).

The present study focused on three abandoned mines with different locations in the Iberian Peninsula to evaluate the influence of ore deposits, paragenesis, and climate diversity on AMD properties. The main objectives are understanding the spatial distribution, seasonal behavior, and relationship between pollutants in different AMD-affected systems.

Methods

Three mining sites with different geographic, climate, paragenetic, and rehabilitation states were selected: Valdarcas (W mine in a skarn deposit, northern Portugal); São Domingos (massive sulfides in the Portuguese sector of the IPB); and Campanario (Cu mine in the Spanish sector of the IPB). Fig. 1 shows the location of the mining areas and respective sampling sites. Table 1 presents a summary of some aspects of these mines.

Sampling occurred during the hydrological year of 2018/2019, measuring in situ parameters (pH, electrical conductivity (EC), redox potential (Eh), and temperature). Thermo Scientific Model Orion Star A Series) combined with a pH electrode triode (Orion 9107BNM) and conductivity cell (Orion

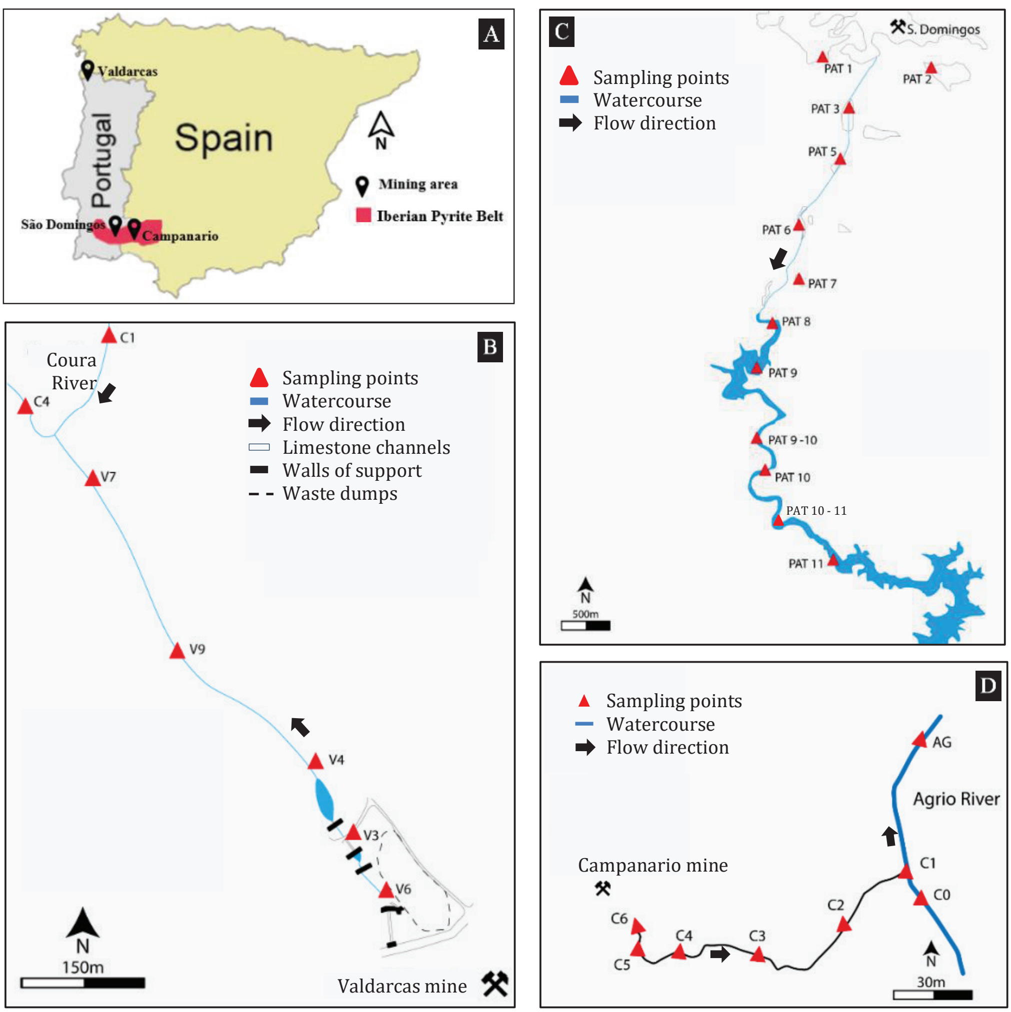

Figure 1 Location of three case studies. A: Selected mines in the Iberian Peninsula. B: Sampling sites in Valdarcas; C: Sampling sites in São Domingos; D: Campanario

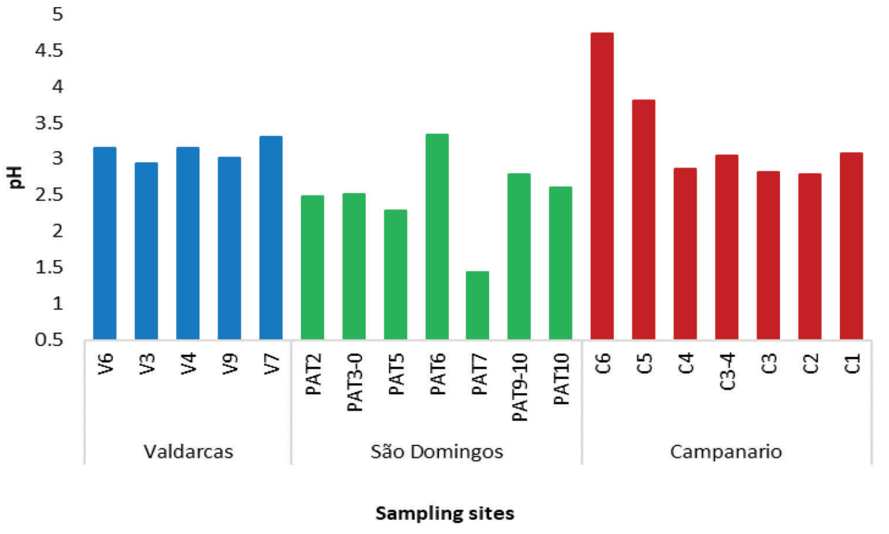

Figure 2 Annual average pH (N = 12) measured in the hydrological year 2018–2019 for the three studies cases

01310MD) was used for field measurements. Redox potential (Eh) was measured using an ORPTestr 10. Samples were analyzed for sulfate (turbidimetry), acidity/alkalinity (volumetry), and potentially toxic elements (PTE) (inductively coupled plasma mass spectrometry after filtration and acidification with HNO_3). Iron speciation was obtained using the Standard 3500 D-phenanthroline method (APHA 2012). At each sampling site, filtered (< 0.2 µm) and unfiltered samples were prepared to compare dissolved and total concentrations of PTE. Supergenic products, such as ochre precipitates and salt efflorescences associated with these waters, were also collected and analyzed for chemistry and mineralogy.

Results and discussion

Figs. 2 to 4 represent some AMD indicators for the three sites. The pH is below 5, with most samples between 2 and 3. Valdarcas presents a pH of around 3 in the sampling points of the receiving watercourse. The highest pH occurs in the Campanario mine, at the base of the waste dump (C6). At the same time, the lowest was observed in the industrial area of Sa o Domingos (PAT7) with pH < 2 (fig. 2).

Table 1 General characterization of the three case studies

Study areas	Location	Climate		Operation and mineralization	State/ rehabilitation
		Temperature (°C)	Precipitation (mm)		
Valdarcas	Northern Portugal	15	1695	Began in 1954; W in a skarn with sulfides	Closed in 1984/ rehabilitated between 2005 and 2007
São Domingos	The Portuguese sector of the IPB	10.4 - 25.7	515	Cu, Ag and Au in roman times; Cu, Zn Pb, and pyrite in the 19th and 20th centuries; Massive sulfides	Closed in 1966/ rehabilitation in course
Campanario	The Spanish sector of the IPB	18	553	20th century between 1906 and 1917; Cu; Massive sulfides	Closed in 1917/ without rehabilitation project

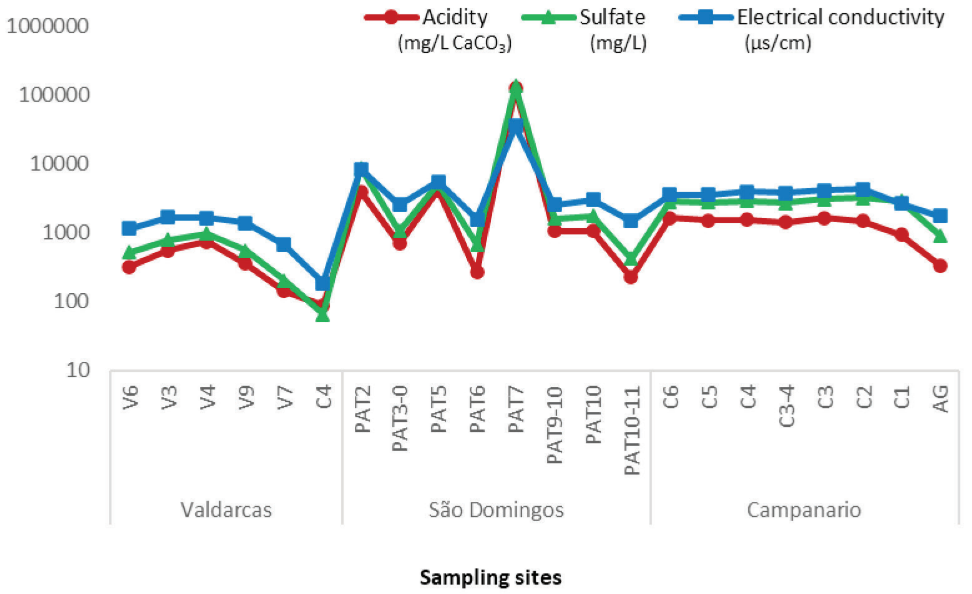

Figure 3 *Annual average electrical conductivity, acidity, and sulfate concentration (N = 12) for the three study cases in the hydrological year 2018–2019*

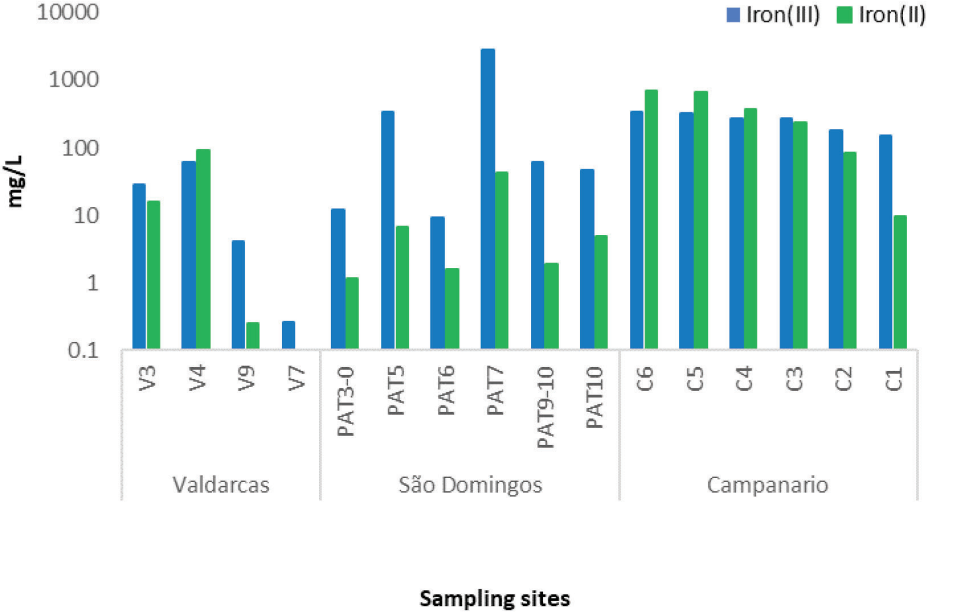

Figure 4 *Annual average concentration of Iron (II) and Iron (III) (N = 12) in the hydrological year 2018–2019 for the three study cases*

Acidity, sulfate, and electrical conductivity present high values, with a maximum in Sa o Domingos, at PAT7 (fig. 3).

These indicators reveal typical characteristics of AMD, although with some differences in magnitude. The sampling points with the highest concentrations occur in Sa o Domingos and the lowest in Valdarcas. In Valdarcas, sampling point C4 represents the effect of natural attenuation from mixing with the Coura River water (fig. 1B).

In general, samples present high redox potential, which is reflected in iron speciation (fig. 4). In the Valdarcas mine dominates the Iron (III), except V4. In Sa o Domingos, Iron (III) is higher in all sampling sites, with redox potential reaching a maximum of 588 mV. In Campanario, the most reducing conditions are found at point C6, in agreement with the dominance of Iron (II) and the lowest redox potential (207 mV). As the flow progresses from C6 to C1 (fig.1), oxidation and hydrolysis occur, and therefore the Iron (III) justifies this behavior.

The hydrochemical characteristics observed at each site are linked to their distinct supergenic mineralogical associations. In Valdarcas, the predominant minerals are iron oxyhydroxides and hydroxysulfates, particularly schwertmannite (abundant in V4) and goethite (V7). Following the environmental rehabilitation project, salt efflorescences decreased, with gypsum and occasionally rozenite being the only remaining representatives (found along the stream banks in V6 and V4 in dry periods). Sa o Domingos exhibits a high prevalence of jarosite, aligning with the recorded low pH values (pH ≤ 3). As documented in prior studies (Gomes et al., 2017), salinization is a recurrent phenomenon involving sulfates of iron, magnesium, and aluminum, such as copiapite, melanterite, and epsomite. Contrastingly, in Campanario, the broader range of pH levels is accompanied by various products, including jarosite in sites with lower pH, schwertmannite, goethite (≈3.0), and basaluminite (pH ≈ 4.5). Copiapite is notably abundant alongside these products.

The Ficklin classification shows that most AMD samples are acid or high-acid and high metal. The near-neutral samples correspond to the backgrounds of each mine site.

Results differentiate between the three sites' regional backgrounds and mine-influenced waters. The pH, EC, Eh, and acidity and sulfate concentrations indicate the highest aquatic ecosystem degradation in the Sa o Domingos mine, where there is a large accumulation of very fine sulfide-rich wastes. The effect of natural attenuation, especially by dilution and precipitation, is

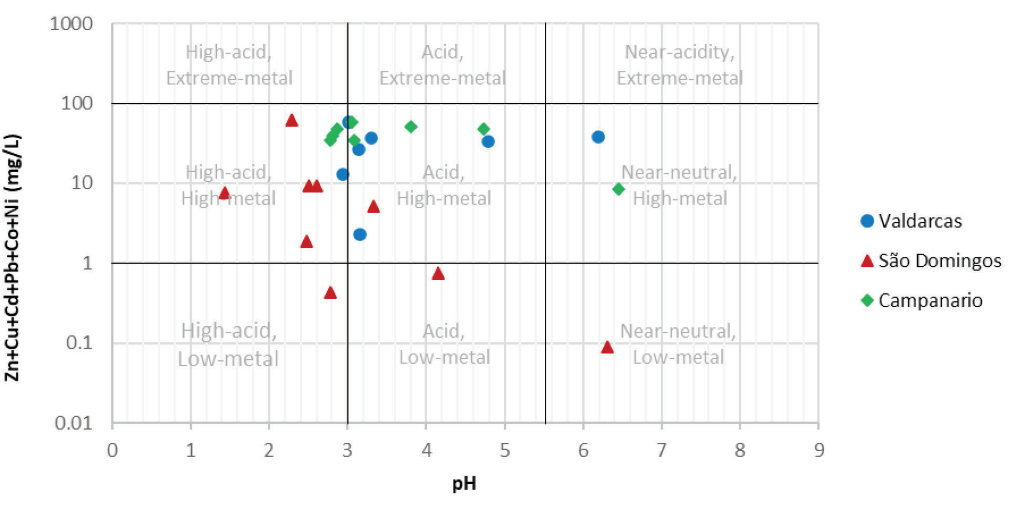

Figure 5 Ficklin diagram (Ficklin et al., *1992) with the classifications of the samples from the three case studies*

also verified in Valdarcas. Eh values agree with the concentration of iron (III) and iron (II) related to oxidation-reduction reactions (fig. 4). Different contamination ranges can be observed, with the Ficklin diagram giving high-acid, acid, and high-metal or low-metal classifications (fig. 5).

Different paragenetic contexts reflect distinct contamination levels. The IPB's volcanogenic massive sulfides contribute to the most compromised scenarios, showcasing worsened degradation in Sa o Domingos. Campanario is also situated in the IPB, but metallurgical practices were more artisanal, resulting in coarser waste materials. These differences and local lithological and paragenetic variations contribute to the distinctive features that set apart these two mining sites. On the other hand, the least extreme values for the parameters under analysis are observed in completely different geology and climate, like the skarn-type deposit of Valdarcas.

Conclusion

Although there are different climate conditions and AMD sources in the three study cases, the relationships between indicators are similar. Nevertheless, the magnitude of contamination is different, with maximum degradation in the Sa o Domingos mine. Seasonal variation is more pronounced in Valdarcas and is related to climate variety and rainy periods. Also, the presence of carbonates and calcium silicate minerals (associated with the skarn) promotes neutralization reactions with the precipitation of ochre products. However, this is not enough to avoid contamination by AMD at this site, which has a pH of around 3. This study illustrates the need for efficient monitoring and remediation protocols, even in sites already submitted to rehabilitation, such as the Valdarcas mine.

Acknowledgments

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