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Long term fluctuations of groundwater mine pollution in a sulfide mining district with dry Mediterranean climate: Implications for water resources management and remediation

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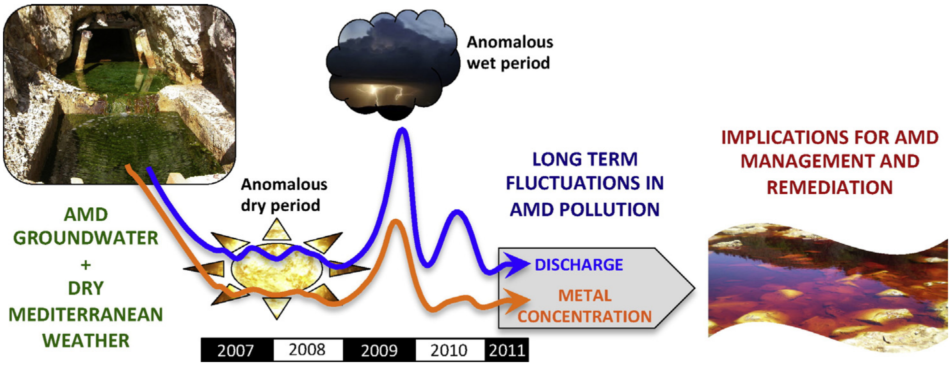
HIGHLIGHTS

- Dry Mediterranean climate induces marked long-term fluctuations in AMD hydrochemistry.
- Precipitation of evaporitic salts within the galleries acts as a metal reservoir.
- AMD remediation strategies must be preceded by at least 5 years of AMD monitoring.
- New modular semi-passive treatments are required to face AMD long-term fluctuations.
- The aggravating effect of climate change must be included in AMD remediation designs.

GRAPHICAL ABSTRACT



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ABSTRACT

Water resources management and restoration strategies, and subsequently ecological and human life quality, are highly influenced by the presence of short and long term cycles affecting the intensity of a targeted pollution. On this respect, a typical acid mine drainage (AMD) groundwater from a sulfide mining district with dry Mediterranean climate (Iberian Pyrite Belt, SW Spain) was studied to unravel the effect of long term weather changes in water flow rate and metal pollutants concentration. Three well differentiated polluting stages were observed and the specific geochemical, mineralogical and hydrological processes involved (pyrite and enclosing rocks dissolution, evaporitic salts precipitation-redisolution and pluviometric long term fluctuations) were discussed. Evidencing the importance of including longer background monitoring stage in AMD management and restoration strategies, the present study strongly advise a minimum 5-years period of AMD continuous monitoring previous to the design of any AMD remediation system in regions with dry Mediterranean climate.

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1. Introduction

Acid mine drainage is the term conventionally used to refer the metal pollution and physico-chemical behavior characterizing waters that have been in contact with acidity producing minerals (e.g., sulfides or Fe oxides and hydroxides) in mining districts. These waters exhibit several peculiarities, viz: high metal and sulfate concentration, low pH values and to be commonly buffered by the precipitation of Fe (e.g., schwertmannite) or Al (e.g., hydrobasaluminite) minerals (Bigham and Nordstrom, 2000). Moreover, AMD pollution is a worldwide and recalcitrant environmental problem affecting both surface waters and groundwater that typically endures for centuries or even millennia (Younger et al., 2002).

AMD hydrochemistry might be significantly influenced by seasonal fluctuations (Kim and Kim, 2004; Olías et al., 2004; Cánovas et al., 2008). Therefore, it is reasonable to expect serious effects of global climate change in AMD pollution that are difficult to predict (Nordstrom, 2009). The effect of seasonal variations in the pollution of surficial AMD has been widely studied, revealing a clear correlation between drought/wet periods and AMD metal concentration. In this regard, it has been repeatedly documented that the first storm event after a drought period induces a sudden increase in surficial AMD acidity and metal load (Nordstrom, 2009, Kimball et al., 2007, Cánovas et al., 2010). This effect has also been reported as “first flush” and it is attributed to the dissolution of the efflorescent salts that typically cover riverbanks during the dry season. The following storm event of the wet season commonly produces a slight dilution in metal concentration and a pH increase, slightly improving water quality (Cánovas et al., 2010). These seasonal variations can also be recorded as sequences of precipitates within the sediments of AMD affected rivers (Caraballo et al., 2011a, 2011b).

The aforementioned “first flush” concept is also applied to groundwater emerging to the surface during the first months following the closure and subsequent flooding of an underground mine (Gzyl and Banks, 2007; Younger, 1997). Most research effort has been placed on the study of AMD groundwater in coal mining districts (Jarvis et al., 2006; Lambert et al., 2004; Younger, 2000; Younger et al., 2002; and papers therein). Whereas only a few studies have looked into groundwater hydrochemical variations in sulfide mining districts (Gray, 1998; Nordstrom et al., 2000). In coal districts, the longevity of the “first flush” effect or “vestigial acidity” in the galleries has been estimated to be around 40 years, while the persistence of “juvenile acidity” (due to the dissolution of all the remaining pyrite in the galleries) could extent along hundreds of years (Younger, 1997, 2000). The acidity and metal concentration of the AMD emerging from coal underground mines has been observed to decrease with the time elapsed since the mine closure. This knowledge is essential to design rational planning for the remediation of this devastating pollution.

On the other hand, AMD pollution in sulfide mining districts is commonly more severe in terms of metal concentration and most importantly in terms of its longevity (Bigham and Nordstrom, 2000). This extreme longevity is due to the enormous amount of pyrite and other sulfides remaining in the galleries of the abandoned mines. In some sulfide mine districts, like the Iberian Pyrite Belt (IPB, SW Spain), the emerging waters from the underground mines correspond to almost 40% of the AMD discharges catalogued in the region (Sánchez-España et al., 2005). A good understanding of both seasonal variations and inter-annual drought and flood events on AMD hydrochemistry is crucial to estimate the intensity and evolution of this pollution and, subsequently to design efficient remediation strategies to accommodate all the system fluctuations over time.

The current research analyzes the results obtained after more than 4 years monitoring the emerging waters from the adit of an abandoned underground pyrite mine. The relationship between the local rainfall regime and weather, the flow rate at the adit and the evolution of AMD metal load is discussed. Galleries at abandoned mines are typically inaccessible, so the geochemical and mineralogical processes occurring within them need to be inferred only by the study of the outflowing AMD. To offer some tools enabling a realistic interpretation of such hidden processes, a set of meteorological, hydrogeochemical and mineralogical parameters were combined using various analytical techniques.

2. Methods and sampling procedure

2.1. Site location

The current study was performed in Mina Esperanza, located in the northern part of the IPB in South-western Spain (37°45′34″N-6°41′00″ O) (Fig. 1). The mineralization at Mina Esperanza consists of a massive pyrite deposit with minor amounts of chalcopyrite (Pinedo-Vara, 1963). The enclosing rocks are slates and low grade metamorphic phyllites. The underground works mined a massive pyrite deposit with chalcopyrite, sphalerite and galena (Pinedo-Vara, 1963). The mine was under operation from 1906 to 1931. After its final closure in 1975, the mine was abandoned, naturally flooded and, subsequently, contaminated water began to flow out of the main adit. As an orphan mine site, there is not any mining company liable for the generated pollution and the mining information available (e.g., underground plans and drawing) is limited or entirely nonexistent.

The pluviometric data were provided by the Spanish Weather Service (http://www.aemet.es) and correspond to the automatic station located in El Campillo, 10 km apart from the Mina Esperanza mining area (Fig. 1).

2.2. Water sampling and analyses

Water samples and flow measurements were taken at least twice a month from March 2007 to October 2008, once every 2 months from November 2009 to January 2011 and at least once a month from February 2011 to June 2011. Sampling gap between November 2008 and October 2009 was due to logistic problems (impossibility to access the sampling points). The samples were filtered immediately after collection through 0.1 μm Millipore filters on Millipore syringe filter holders, acidified in the field to pH < 1 with Suprapur® HNO_3 and stored at 4 °C in 60 mL sterile polypropylene containers until analyzed.

Temperature and electrical conductivity were measured using a portable CM35 meter (Crison®) with 3 point calibration (147 and 1413 μS/cm and 12.88 mS/cm). The pH and redox potential were measured using a PH25 meter (Crison®) with Crison electrodes. Redox potential and pH were controlled and calibrated using 2 points (240–470 mV) and 3 points (pH 4.01–7.00–9.21), respectively, with Crison® standard solutions. Redox potential measurements were corrected to the Standard Hydrogen Electrode to calculate pe.

In order to obtain a better understanding of the different processes controlling the outflowing water chemistry, a representative sample from the final period of study was submitted to an evaporation process. The hydrochemistry evolution during the evaporation process and the evaporitic salts generated were analyzed in detail. In addition, the evaporation process was reproduced and studied by means of a geochemical model. A detailed description of the evaporation experiment and modeling is offered in the supplementary information.

The concentration of dissolved Fe, Cu, Zn, Na, Al, Ca, Mg, and S in solution was measured by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) with detection limits of 10 μg/L for Fe, Cu and Zn, 100 μg/L for Na and 50 μg/L for Al, Ca, Mg and S. The concentrations of As, V, Sr, Cd, Pb, Ni and Co were determined by Inductively Coupled Plasma Atomic Mass Spectroscopy (ICP-MS) with detection limits consistently on the order of 1 μg/L. Detection limits were calculated considering the mean signals and standard deviations of a blank measured ten times. In the ICP-AES and ICP-MS analyses, calibration with sets of standards was performed at the beginning and at the end of each ten-samples analytical series. Certified Reference Material SRM-1640NIST fresh-water-type and inter-laboratory standard IRMM-N3 wastewater