Spatial distribution of acid mine drainage indexes in different water environments

I. M. H. R. Antunes¹, T. M. F. Valente¹, P. Gomes¹, M. R. Costa², R. Fonseca³, F. Moreno¹

¹ ICT, University of Minho, Campus de Gualtar, 4710 - 057 Braga, Portugal, imantunes@dct.uminho.pt; teresav@dct.uminho.pt; patricia_s_gomes@hotmail.com; filipa_moreno@hotmail.com

² GEOBIOTEC, University of Trás-os-Montes and Alto Douro, Quinta de Prados, 5000-801 Vila Real, Portugal, rosario.costa@utad.pt

³ ICT, University of Évora, Department of Geosciences, Évora, Portugal

Abstract

The Iberian Pyrite Belt is one of the largest metallogenic province in the world. The characteristics of this region have a reflection on the existence of Acidic Mine Drainage (AMD) discharged into the river network affecting the water quality.

A several number of surface and groundwaters in the Iberian Pyrite Belt (south of Portugal) was collected in different water environments. Mine water is highly acid with medium-high to extreme metal contents, while surface and groundwater are neutral with low metal contents. Mine waters are the most contaminated with a maximum EC value (27570 μ S/cm) and SO₄⁻² (80691 mg/L), As (141 mg/L), Cu (1445 mg/L), Fe (41023 mg/L), Zn (841 mg/L) contents.

A numerical index of acid mine drainage (AMDI) has been calculated. The group of mine water environment had a mean AMDI of 20.0 reflecting a little or no dilution of direct mine water drainage. River network could be indicated as an affected river downstream mine drainage (AMDI 80.2), while groundwater (AMDI 92.2) is uncontaminated by AMD. The groundwater composition will be strongly controlled by natural geochemical processes, from the geology of the ore deposits and water rock interaction.

Keywords: surface, groundwater, acid mine indexes, contamination, monitoring

Introduction

The incessant mining activity since Roman times promoted numerous abandoned and active mine sites that are an important source of water contamination. Nowadays, there are more than 4800 ha occupied by waste dumps, open pits, tailing dams, and mining facilities (Grande et al. 2013). Some of these mines can be considered representative of the paragenetic diversity as well as of mining history and environmental framework of the Iberian Pyrite Belt (IBP), in southwestern Europe, one of the most important metallogenic provinces in the world. In this metallogenic province, which covers a large area of cross-border territory between Portugal and Spain, most of the mines were closed without environment guidelines and without preventive or corrective measures to protect the environment (Rodrigues 2011;

Grande et al. 2013).

Water is a key resource for human living, especially for drinking and irrigation purposes and its quality is one of the most critical factors influencing human health (Zhang et al. 2012). Water protection is a major management concern, particularly in scenarios of water scarcity and water contamination, especially in mining regions with semi-arid climates. The studied area is one of the driest regions of southwestern Europe, with precipitation occurring mostly in the winter months, and droughts frequently occurring during the summer (Gomes et al. 2018).

One of the most serious problems of environmental contamination worldwide is the formation of acid mine drainage (AMD) in mining regions. The general process of AMD formation results from a series of interconnected steps that are primarily accomplished by oxidation of sulphides (Lottermoser 2010). Sulphide minerals are exposed to weathering, which generates acidity, sulfate and potentially toxic elements (e.g., Valente et al. 2015; Gomes et al. 2016; Soyol-Erdene et al. 2018). The leachates emerging from waste dumps, tailings dams, and other mining facilities are discharged into the river network, being responsible for the contamination of the receiving water courses (Valente et al. 2013; Gomes et al. 2018).

There is a considerable difficulty in comparing temporal and spatial variation of AMD wastewaters, and affected surface and groundwaters, using individual chemical and physical parameters. The effect of AMD on the different water systems is also complex due to the multi-factor nature of the effects (Kelly 1988). Slight variations in environmental conditions can cause substantial differences in individual parameter flux rates. Therefore, acid mine drainage index (AMDI) is very important to detect, quantify and categorize water quality and to monitor the recovery of contaminated sites (Kuma et al. 2011).

The present study aims to study the occurrence of some potentially toxic elements in different spatial water environments in the semi-arid climate Portuguese metallogenetic province of the IPB and the application of the acid mine drainage index. This index allows for the contamination detection and its quantification from acid mine drainage and consequently to monitor the recovery of receiving waters.

Methods

The study area is in the southwest region of the Iberian Peninsula, covering the Portuguese sector of the Iberian Pyrite Belt (IPB). This region is part of a geological formation with a high density of polymetallic sulphide deposits which extends from Seville (Spain) to the coast of Portugal (Fig. 1).

The IPB is subdivided into several tectonostratigraphic units including the Phyllite-Quartzite (PQ) Group and the volcano-sedimentary complex (VSC) (Sáez et al. 1999). The presence of more than 90 polymetallic sulphide deposits associated with the volcano-sedimentary complex gives to the Pyrite Belt a status of being a worldclass metallogenic province (e.g., Relvas et al. 2002). The massive sulphide deposits contain predominantly pyrite, sphalerite, galena and chalcopyrite, and are associated with many minor phases (Sáez et al. 1999). The geological and mineralogical characteristics of the region reflect the existence of AMDproducing wastes that are dispersed by the numerous mining complexes and once discharged into the river network, and may affect the quality of water bodies (Gomes et al. 2018).

A total of twenty-one surface and groundwater samples in the IPB (south of Portugal) was collected and analysed for physico-chemical properties and selected trace elements. Water sample sites were categorized into three similar groups based on source classification: mine water environments (10 samples), river network (6 samples) and



Figure 1 Location of the study area in southwestern Portugal.

groundwater (5 samples). Temperature, pH, redox potential (Eh), Total Dissolved Solids (TDS) and Electrical Conductivity (EC) were measured "in situ". The collected samples were transported to the laboratory and the anions were determined by ion chromatography, while metals and arsenic were analysed by inductively coupled plasma optic spectrometry spectrometry (ICP-OES).

Numerical indices of the severity of acidic mine drainage have been calculated for the three different water environments of the study area. The acid mine-drainage index (AMDI; Gray 1996) is calculated using a modified arithmetic weighted index utilizing seven parameters (qi) which are most indicative of acid mine-drainage contamination, i.e. pH value, sulphate, iron, zinc, aluminium, copper and cadmium. Weighting (wi; Table 1) express the relative indicator value of each parameter, estimated by consideration of (a) the concentration of parameters in raw and diluted AMD, (b) their sorption properties, (c) the effect of neutralization on concentration, (d) the relevance of concentration to ADM formation, and (e) detection limits of the analytical procedures used (Nieva et al. 2018). The pH and sulphate are considered to be of highest indicator value as they were unaffected by sorption processes, while sulphate was also unaffected by neutralization processes and by natural neutralization (Gray 1996). The AMDI score is calculated according to the equation: AMDI = $[\Sigma (qiwi)]^2/100$ (Gray 1996), where qiwi are the water quality ratings of the seven parameters.

The water quality (q) for each parameter is measured on a scale from 0 to 100, with values

closer to 0 corresponding to the raw AMD or to highly contaminated waters and 100 to the best possible quality. However, the problem with this approach is that it lacks sensitivity in the effect which a single bad parameter value will have on the water quality index (Gray 1996).

Results

Mine water is highly acid (pH 1.8-3.6) with medium-high to extreme metal contents, while surface water (pH 6.6-7.7) and groundwater (pH 7.2-8.0) are neutral with low metal contents (Fig. 2). There is no significant difference between the chemical composition of surface and groundwater suggesting a low residence time, therefore surface waters show a high metal content (Fig. 2).

However, all the waters are extremely mineralized with an electrical conductivity mean value of 8926, 1262 and 1136 μ S/cm, in mine waters, surface water and groundwater, respectively. Mine waters are the most contaminated with a maximum EC value of 27570 μ S/cm and SO₄⁻²⁻ (80691 mg/L), As (141 mg/L), Cu (1445 mg/L), Fe (41023 mg/L), Zn (841 mg/L) contents. These waters are contaminated and cannot be used for human consumption or agricultural irrigation according to the Portuguese parametric values (Portuguese Decree 1998; 2007).

The piper classification shows a set of samples that are mainly sulphate waters (magnesium and mixed sulphate-types), corresponding to the AMD-affected waters (Gomes et al. 2018). Surface freshwaters present higher variability and are mainly mixed chloride and sulphide. Groundwaters are mixed chloride suggesting a water rock interaction.

Parameter identifier (i)	Parameter	Weighting (wi) 0.20	
1	рН		
2	Sulphate (mg/L)	0.25	
3	Iron (mg/L)	0.15	
4	Zinc (mg/L)	0.12	
5	Aluminium (mg/L)	0.10	
б	Coper (mg/L)	0.08	
7	Cadmium (µg/L)	0.1	
	Total weighting	1.0	

Table 1. Parameters and weightings used in the calculation of ADMI (Kuma et al. 2011).



Figure 2 Projection of the studied waters in the Ficklin et al. (1992).

Table 2. AMDI variability of the different water environments from the studied area

Water environments	ADMI				
	Mean	Minimum	Maximum	SD	n
Mine environments	20.0	1.7	39.7	14.0	10
River network	84.6	74.0	86.5	6.4	7
Groundwater	95.1	88.4	96.0	3.6	5

SD - standard deviation; n - number of samples.

The ADMI index was calculated considering the most indicative parameters of AMD contamination (qi – pH, SO₄²⁻, Fe, Zn, Al, Cu and Cd) and their respective weightings (wi) of the water from mine water environments. river network and groundwater (Table 2). The group of mine water environments had a mean AMDI of 20.0 (1.7 - 39.7) reflecting a raw ADM with little or no dilution of direct mine water drainage, mainly seepage from spoil collecting in surface ponds. According to the classification of contaminated and uncontaminated waters by AMDI (Gray 1996), river network could be indicated as an affected river downstream of the mine drainage (AMDI: 74.0 - 86.5), while groundwater (AMDI: 88.4 - 96.0) is uncontaminated by AMD. The groundwater composition will be strongly controlled by natural geochemical processes, from the geology of the ore deposits and water rock interaction.

Conclusions

The acid mine-drainage index is designed to detect and quantify contamination from acid mine drainage, and to help categorize samples, quantify effect and to monitor the recovery of receiving waters. The ADMI index is a tool to discriminate between sources and types of AMD and assessing the degree of effect on surface and groundwaters.

ADMI is also a useful method to quantitatively assess the relative intensity of contamination and effect of acid mine drainage, over time and space, that must be considered in environmental risk assessment of active and abandoned mine sites, before and along remediation and monitoring processes.

Acknowledgements

This work was co-funded by the European Union through the European Regional Development Fund, based on COMPETE 2020 - project ICT (UID/GEO/04683/2013) with reference POCI-01-0145-FEDER-007690 and project Nano-MINENV number 029259. The authors are grateful to the suggestions of the reviewers.

References

- Ficklin WH, Plumlee GS, Smith KS, McHugh JB (1992) Geochemical classification of mine drainage and natural drainage in mineralized areas. In Kharaka YK, Maet AS (Eds.), Waterrock interaction 7:81-384
- Gomes P, Valente T, Pereira P (2018) Addressing quality and usability of surface water bodies in Semi-arid regions with mining influences. Environm Proc, doi: 10.1007/s40710-018-0329-0
- Gomes P, Valente T, Sequeira Braga MA, Grande JA, de la Torre ML (2016) Enrichment of trace elements in the clay size fraction in mining soils. Environm Sci Pollut Res 23(7):6039-6045, doi:10.1007/s11356-015-4236-x
- Grande JA, Santisteban M, de la Torre ML, Valente T, Pérez-Ostalé E (2013) Characterization of AMD pollution in the reservoirs of the Iberian Pyrite Belt. Mine Water Environ Geochem 32:321-330, doi:10.1007/s10230-013-0236-6
- Gray NF (1996) The use of objective index for the assessment of the contamination of surface water and groundwater by acid mine drainage. J Chart Inst Water E 10:332-341
- Kelly MG (1988) Mining and freshwater environment. Elsevier Applied Science, London
- Kuma JS, Younger PL, Buah WK (2011) Numerical indices of the severity of acid mine drainage: broadening the applicability of the Gray Acid Mine Drainage Index. Mine Water Environm 30:67-74, doi: 10.1007/s10230-010-0133-1
- Lottermoser BG (2010). Mine Wastes: Characterization, Treatment, Environmental Impacts. Springer, 315.
- Nieva EN, Borgnino L, García MG (2018) Long term metal release and acid generation in abandoned mine wastes containing metalsulphides. Environm Pollut 242:264-276,

https://doi.org/10.1016/j.envpol.2018.06.067

- Portuguese Decree (1998) Decreto-Lei 236/98 Legislação Portuguesa de Qualidade da água. Diário da República I-A: 3676-3722
- Portuguese Decree (2007) Legislação Portuguesa de Qualidade da água. Diário da República I-A: 5747-5765
- Relvas JMRS, Barriga FJAS, Pinto A, Ferreira A, Pacheco N, Noiva P, Barriga G, Baptista R, Carvalho D, Oliveira V, Munhá J, Hutchinson R (2002) The Neves-Corvo deposit, IPB, Portugal: 25 years after the discovery. Soc Econ Geol, Special Publication 9:155-176.
- Rodrigues R, Coord. (2011) A herança das minas abandonadas – o enquadramento e atuação em Portugal. EDM – DGEG, p 180, http://www. edm.pt/html/livro.html#/14/
- Sáez R, Pascual E, Toscano M, Almodovar G (1999) The Iberian type of volcanosedimentary massive sulphide deposits. Mineral Dep 34:549-570
- Soyol-Erdene TO, Valente T, Grande JA, de la Torre ML (2018) Mineralogical controls on mobility of rare earth elements in acid mine drainage environments. Chemosphere 205: 317-327, https://doi.org/10.1016/j. chemosphere.2018.04.095
- 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
- Valente T, Grande JA, de la Torre ML, Gomes P, Santisteban M, Borrego J, Sequeira Braga MA (2015) Mineralogy and geochemistry of a clogged mining reservoir affected by historical acid mine drainage in an abandoned mining area. J Geochem Explor 157:66-76, https://doi.org/10.1016/j.gexplo.2015.05.016
- Zhang B, Song X, Zhang Y, Han D, Tang C, Yu Y, Ma Y (2012) Hydrochemical characteristics and water quality assessment of surface water and groundwater in Songnen plain, Northeast China. Water Res 46:2737-2748, https://doi. org/10.1016/j.watres.2012. 02.033