Restoration measures of an AMD polluted watershed based on mixing and geochemical models

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Abstract This work studies the implementation of a simple mixing and geochemical model to assess the adoption of remediation measures in a highly AMD impacted watershed in SW Spain. The model provides a good snapshot of the impact of potential passive treatment plants on the water quality amelioration of this basin. The implementation of these plants in selected sites would reduce notably the level of metals in the watershed (e.g. from 92 to 99% of Fe and Cu). However, this is a preliminary approach and a more detailed study of each mine site is required to obtain a cost-effective restoration of this watershed.

Key words metal pollution, PHREEQC, Fe precipitation, predictive tools

Introduction

The Directive 2000/60/EC of the European Parliament, so-called Water Framework Directive (WFD), established a communitarian frame of action in the scope of water policy, whose main objective was to achieve a good ecological and chemical quality of all European waters by 2015. The WFD allows the deadline prolongation in cases of technical difficulty, when improvements within the timescale would be economically unsustainable and if natural conditions do not foster the timely improvement. This is the case of the Sancho Reservoir (58 Mm^3 of storage capacity), located in the Meca River basin, within the Iberian Pyrite Belt (IPB, SW Spain), which is an extreme case of acid mine drainage (AMD) pollution worldwide. The reservoir water quality has suffered a progressive worsening especially since 2007 due to increasing AMD pressure, yielding low pH values (around 3.5) and high levels of sulfate and metals (Cánovas et al. 2016). The WFD fosters the development of new approaches to assess the impacts of restoration measures on the water quality. This assessment has been previously performed by mass balance approach and reactive transport models (e.g. Kimball et al. 2002 and 2009; Runkel et al. 2007). However the methodology employed in these studies may be expensive, complex and time consuming (i.e. tracer injection tests, synoptic samplings, reactive transport modelling). This work studies the implementation of a mixing and geochemical model to assess the adoption of environmental and cost-effective remediation measures.

Methods

Site description

The Meca River basin has an area of 315 km^2 and partially drains the mining district of Tharsis (Fig. 1A), one of the largest of the IPB comprising 16 massive sulfide lenses with original reserves of around 133 million tons (Cánovas et al. 2016). The intense mining activities developed especially from the mid-nineteenth century to the late twentieth have left an extensive area of flooded open-pits, galleries, shafts and mining wastes (Fig. 1) that release metals and acidity to the watershed. Prado Vicioso (PV, Fig. 1B) is an underground mine exploited mainly during the 20th century whose acidic leachates together with those arising from surrounding spoil heaps constitute the source of the Meca River. Afterwards, the Meca River collects the drainages from Esperanza deposit (Fig. 1B). The mineral exploitation in this deposit has led to the formation of an open pit, partially filled with mine wastes. The leachates originated from this pit and several waste dumps located to the east are collected in a small dam that subsequently discharges the contaminated water by overflow (sampling point CE, Fig. 1B). Spoil heaps located to the south and southeast of this open pit also release an acidic leachate (sampling point SH, Fig. 1B). Downstream of the Tharsis complex, the Meca River receives the drainages from La Lapilla (sampling point LAP, Fig. 1B). This mine is surrounded by spoil heaps, low grade ore stockpiles and wastes from cyanide heap leaching whose exposure to atmospheric conditions leads to the generation of an acidic drainage.

To the west, there are two AMD-affected streams reaching the Meca River; Tía Sebastiana Creek and Dehesa Boyal Stream which join the Meca River downstream (sampling points DB and TS; Fig. 1A and B). Both water courses are affected by acidic drainages from spoil heaps and underground galleries that worsen irreversibly the water quality. As a result, the Meca River is deeply contaminated by AMD, transporting huge amounts of contaminants to the Sancho Reservoir which has suffered a progressive acidification in the last years (Cánovas et al. 2016).

Sampling and analytical methods

All AMD-sources from the Tharsis and La Lapilla mines were sampled under different hydrologic conditions in order to study the variability of AMD composition. In addition, different non-affected streams (n=4) were also sampled to establish the background chemical composition of freshwaters in the catchment.

Electrical conductivity (EC), pH and oxidation-reduction potential (ORP) were measured *in situ* for all samples using a Crison MM 40+ portable meter. Samples were filtrated through 0.2 μm filter and acidified to pH < 2 immediately after collection, and finally stored at 4ºC until analysis. The chemical analysis were undertaken at the Central Research Services of Huelva University using inductively coupled plasma optical emission spectroscopy (ICP-AES; JY ULTIMA 2) on a Jobin Yvon spectrometer to determine major elements and inductively coupled plasma mass emission spectroscopy (ICP-MS; Agilent 7700) for trace elements. Detection limits were 0.2 mg/L for S, 0.1 mg/L for Na, 0.05 for Fe, K, Mg and Si, 0.02 mg/L for Al, Ca and P, and 1 μg/L for trace elements.

Conceptual design of the mixing and geochemical model

An integrated mixing and geochemical model is proposed to predict the water chemistry under two different scenarios; 1) baseline conditions and 2) after restoration measures. The modeling of baseline conditions is only performed for validation purposes by comparing modeled to measured values of different parameters. The mixing model was initiated using the MIX code (Carrera et al. 2004) to estimate the mixing ratios of each AMD source and the receiving water. The variables must satisfy some conditions to be suitable in mixing models; exhibit a conservative behavior and their values must be significantly different in the extreme components.

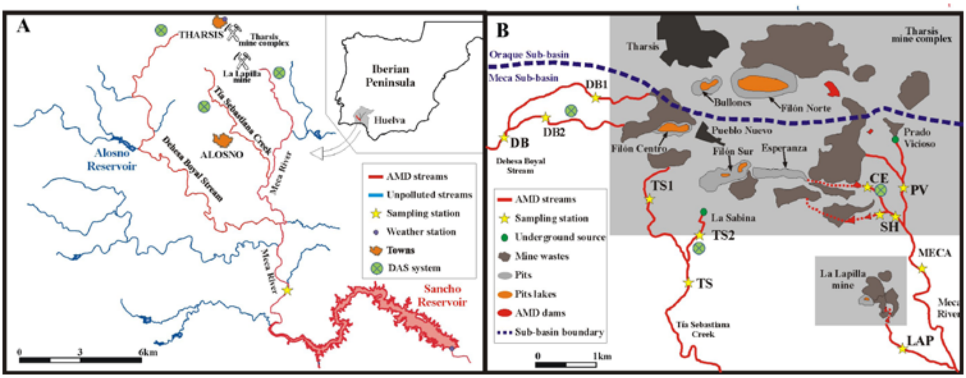

Figure 1 *A) Location map of the watershed showing the streams affected by AMD and B) detailed map of main AMD sources in the watershed.*

The geochemical model applied to the Odiel River was initiated using the "MIX" data block of the PHREEQC code (Parkhurst and Appelo, 1999), from mixing fractions previously obtained by the MIX code. The model is subsequently improved by applying some geochemical constraints using the "EQUILIBRIUM PHASES" data block, which allows phase assemblages to react with an aqueous solution. These geochemical constraints are based on a previous analysis of the saturation state of main minerals commonly found in AMD environments relative to water samples. In this way, some mineral phases found oversaturated in water were forced to reach equilibrium; i.e. schwertmannite and jarosite for Fe minerals; basaluminite and alunite for Al minerals and gypsum. Equilibrated waters are subsequently mixed with downstream inputs, and so on. Modelled values are compared with those measured in real conditions for validation purposes.

The second step is to perform a mixing model including restoration measures in selected sites. Due to the high acidity and metal content of AMD in the IPB, the restoration measure selected is a passive treatment technology known as Dispersed Alkaline Substrate (DAS), which comprises an inert wood shavings matrix to supply high porosity and reduce the clogging problems, mixed with a fine-grained alkaline reagent to increase the substrate reactivity which induces an increase of water pH after dissolution (Macías et al. 2012; Ayora et al. 2013). As a result of the implementation of DAS technology, an acidic (pH 2-3) and metal-rich drainage (more than 300 mg/L of Fe and Zn and around 100 mg/L of Al) is converted in a near-neutral outflow (pH 7 and alkalinity 250 mg/L of $CaCO_3$) depleted of metals.

Results and discussion

As can be seen in Figure 2, a good agreement is observed between modelled and measured concentrations of sulfate, Fe and Al (R^2 = 0.99). In the case of pH, an acceptable agreement is observed between modelled and measured values (R^2 = 0.67), with a group of samples displaying slightly lower modelled values than measured. This is attributed to the equilibrium condition imposed to waters with respect to Fe oxyhydroxysulfates. The precipitation of these minerals causes the release of protons, giving rise to such differences. Nevertheless, an acceptable validation can be considered according to the simplicity of the model.

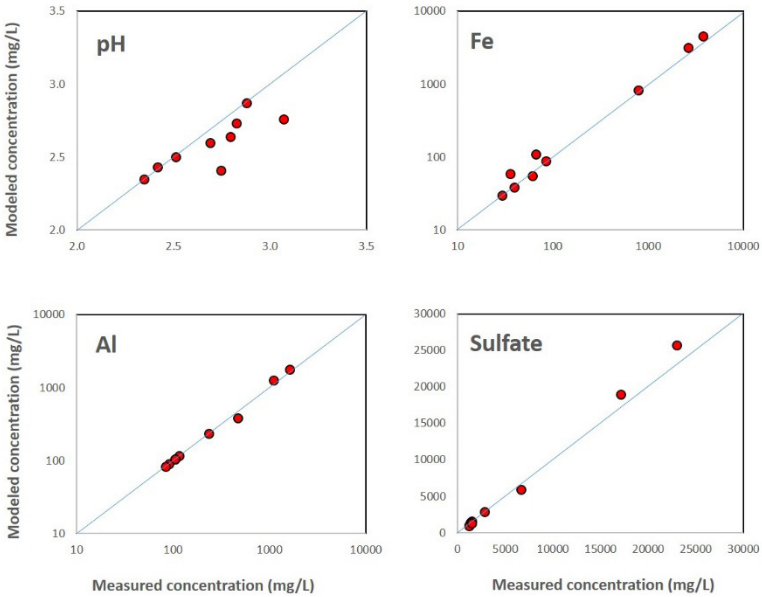

Figure 2 *Validation of the model by comparison of modeled and measured values of selected parameters.*

Once validated, a second model was performed including the implementation of DAS treatment plants in selected sites. The criteria followed to decide the plant locations were the total contribution of each source and the length of the water course potentially restorable. Table 1 shows the average composition of AMD sources studied and their contribution to the total load released to the Meca River. As can be seen, AMD coming from Corta Esperanza (Fig. 1) is the main contributor of Fe (93%), Zn (90%), acidity (78%), sulfate, Al, Cu and Mn (around 70%). The highest flows are generated from mine galleries and spoils heaps located in the drainage basins of Tia Sebastiana Creek and Dehesa Boyal (TS and DB2; Fig. 1) with average values of 9.2 and 5.5 L/s. Both drainages also constitute around 12% of Al, between 10 and 17% of Cu, 8.6 and 11% of sulfate and 2.2 and 3.5% of total Fe. The pollutant load delivered by the rest of AMD inputs is considerably lower (Table 1).

Taking into account these data, the implementation of a DAS treatment plant in each of these sources (CE, TS and DB2; Fig. 1B) was simulated. The implementation of a DAS treatment plant in the vicinity of Corta Esperanza (CE, Fig. 1) to treat their highly metal-rich effluents (Table 1) causes the removal of around 99% and 97% of total Fe aand Zn, respectively, at the end of the river reach (downstream of PV and SH, Fig. 1). Lower removal is observed for Al (94%), Mn (91%) and Cu (90%) due to the contribution of non-treated effluents dowstream of Corta Esperanza (PV and SH, Fig. 1). The lowest removal rate is achieved for sulfate (32%, Fig. 3) due to only a minor fraction of this pollutant is retained in DAS systems by geochemical reactions, i.e. schwertmannite, basaluminite and gypsum precipitation (Macías et al. 2012). Despite the notable removal of pollutants this river reach would not acquire pH values close to neutrality (from pH 2.4 to 3.9; Fig. 3).

Table 1 *Average values (n= 3) of main AMD sources in the study area and contribution to the total load in the watershed.*

Sample	**Flow**	**pH**	**Acidity**	**Al**	**Cu**	**Fe**	**Mn**	**Sulfate**	**Zn**
	L/s		mg/L $CaCO_3$			mg/L			
DB1	1.8	3.1	476	38	2.4	112	21	1171	10
DB2	5.5	2.6	2841	351	44	197	59	7822	33
PV	0.4	2.8	1729	255	13	20	46	3116	44
SH	0.7	2.3	2451	283	68	122	33	6405	13
CE	2.7	2.2	30229	2289	259	5576	273	61044	786
TS	9.2	2.6	857	93	18	56	10	1325	6.3
LAP	0.5	2.9	197	54	2.4	15	13	1194	13
						Total contribution			
DB1			1.2%	0.90%	0.50%	0.66%	3.4%	1.6%	0.79%
DB2			7.3%	11%	10%	2.2%	16%	8.6%	4.1%
PV			4.5%	2.7%	1.0%	0.13%	3.5%	2.2%	1.8%
SH			6.3%	2.6%	4.8%	0.50%	2.2%	2.1%	0.46%
CE			78%	71%	67%	93%	65%	74%	90%
TS			2.2%	12%	17%	3.5%	9.2%	11%	2.8%
LAP			0.5%	0.70%	0.23%	0.09%	1.4%	1.1%	0.57%

In the case of the effluents reaching the Dehesa Boyal stream (DB1 and DB2), the implementation of a DAS treatment plant in the vicinity of the spoils DB2 (Fig. 1) would remove around 96% and 94% of total Cu and Fe carried by this stream. Lower values were observed for Al (92%), Mn (84%) and Zn (83%; Figure 3). As in the case of the upper reach of the Meca River, only a reduction of 31% in sulfate transport was achieved with the settling of the passive treatment. Notwithstanding, a notable increase in pH values (from 3.9 to 5.7, Fig. 3) would be achieved in this stream after applying restoration measures.

The implementation of a DAS treatment plant in Tia Sebastiana creek to treat the acidic effluents from La Sabina gallery (TS2, Fig. 1) would remove around 92% and 85% of the total Fe and Cu, respectively, carried by the creek. On the contrary, minor amounts of Al (50%), Zn (40%) and Mn (21%) would be removed due to these elements are preferentially delivered by spoil heaps deposited in the vicinity of Filón Centro (TS1, Fig. 1). As a result, pH values would increase from 2.6 to 5.1 in this creek after the implementation of the treatment system (Fig. 3).

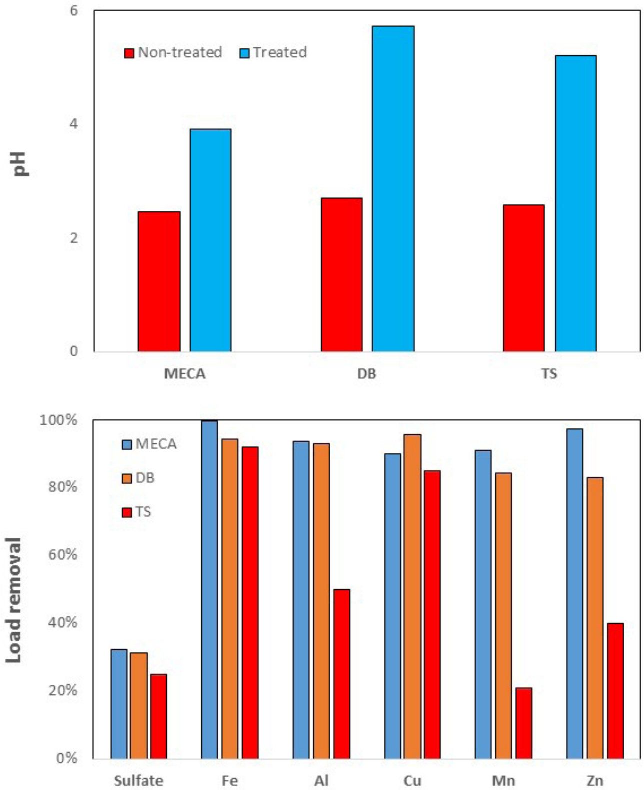

Figure 3 *Modelled results of the impact of DAS treatment plants implementation in selected sites of the study area.*

Conclusions

This study assesses the potential impact of the implementation of passive treatment plants in selected sites of the Meca River Basin (SW Spain), an extreme case of acid mine drainage (AMD) pollution worldwide. The increasing AMD pollution in this basin during the last years has caused the pollution of main water bodies, especially the Sancho Reservoir which has suffered a progressive acidification since 2007. Once validated a preliminary geochemical model of the starting situation, another model was performed to check the possible implementation of treatment plants in selected sites depending on the pollutant load and the length of the water course potentially restorable. AMD coming from Corta Esperanza is the main contributor of Fe (93%), Zn (90%), acidity (78%), sulfate, Al, Cu and Mn (around 70%) while the highest flows are generated from spoils heaps located in the drainage basins of Tia Sebastiana Creek and Dehesa Boyal (average values of 9.2 and 5.5 L/s).

The implementation of treatment plants in Meca headwaters and Dehesa Boyal would reduce the metal level in both catchments between 83% and 99%, respectively. In the case of the treatment plant located in the basin of Tia Sebastiana creek to treat the AMD arising from La Sabina gallery, it will be really effective only for Fe (92%) and Cu (85%) due to this plant would not treat the effluents generated from spoil heaps deposited close to Filon Centro, with high values of Al, Mn and Zn. The settlement of these treatment plants would cause a significant increase in pH values (up to 5.7), although this prediction may have a higher uncertainty than in the case of sulfate and metals due to its poorer validation (r^2 = 0.67). This study proposes a simple tool to predict the impact of restoration measures in watersheds affected by derelict mines. However, more detailed and site-specific studies are required in order to achieve a cost-effective restoration of the watershed.

Acknowledgements

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