Acid Mine Drainage Pollution at the Tharsis Mines (Iberian Pyrite Belt): A Serious Environmental and Socioeconomic Problem

Raúl Moreno-González[1,2], Manuel Olías[1,2], Carlos Ruíz-Cánovas[1,2], Francisco Macías[1,2]

[1]*Department of Earth Sciences, University of Huelva, Avda. Tres de Marzo s/n, 21071, Huelva, Spain*
[2]*Research Center on Natural Resources, Health and the Environment (RENSMA), University of Huelva, Spain raul.moreno@dct.uhu.es, manuel.olias@dgyp.uhu.es, carlos.ruiz@dgeo.uhu.es, francisco.macias@dgeo.uhu.es*

Abstract
The Tharsis mining district belongs to the Iberian Pyrite Belt (IPB), which is rich in massive sulphide deposits. Large-scale mining began in 1866 and continued until 2001, leaving a large area of sulphide-rich dumps, soils affected by mining and 4 pit lakes containing 5.2 hm^3 of acidic waters. The acid mine drainages (AMDs) generated in this area cause a serious environmental and socio-economic problem by producing severe pollution of 115 km of river courses, 58 hm^3 of reservoir waters and compromising the water quality of another large reservoir (246 hm^3) under construction. Measures to reduce the pollution levels should be taken.

Keywords: Water pollution, sulphides, abandoned mines, pit lakes

Introduction
The Tharsis mining district is located in the IPB, specifically in the province of Huelva (SW Spain). The area has gentle relief, with altitudes between 150 and 362 m. The climate is Mediterranean, with an average rainfall close to 600 mm. Most rainfall occurs in autumn and winter while summers are hot and dry. There is also a great interannual variability in rainfall. The most important streams are the 1) Aguas Agrias creek, which drain to the east and flow into the Oraque River and 2) various streams flowing to the south joining finally the Meca River, regulated in its final reach by the Sancho Reservoir (58 hm^3 capacity). Both the Meca and Oraque Rivers belong to the Odiel River basin.

The IPB is very rich in massive sulphide deposits; among them the Tharsis mines is one of the most important, with estimated original sulphide reserves of 133 Mt (Tornos et al. 2009). Exploitation began, on a very small scale, around 4500 years ago. During the Tartessian civilization and the Roman period, extractions were increased through underground mining. After the Roman period followed a long time with little mining activity until 1866, when mining suffered a great development, on an unprecedented scale in the region, in order to obtain copper. At that time, open-pit mining began in Filón Norte and later in Sierra Bullones and Filón Centro (Fig. 1). Underground mining also continued, mainly in the Sierra Bullones area. From the beginning of the 20th century, once the Cu-rich enrichment zone was exhausted, the main objective of exploitation became sulphur for the manufacture of sulphuric acid. In addition, between 1937 and 1964 exploitation of the gossans from Filón Sur to extract gold and silver by cyanidation took place (Tornos et al. 2009). In 1966 the underground mining in Sierra Bullones was definitively abandoned, after 100 years of intense exploitation. From then on, open-pit mining restarted in the Filón Norte open pit until the end of the 90s. Finally, between 1990 and 2000 exploitation resumed in Filón Sur to obtain gold and silver from the gossan. The Tharsis mines have been the second most important of the IPB, after the Río Tinto mines. Since 1866, 40 Mt of sulphides have been extracted (Tornos et al. 2009), to which should be added another 5 Mt from Roman and pre-Roman times (Moreno González et al. 2018).

The sulphide-rich wastes generated in the area produce numerous acid leachates in contact with rainwater and atmospheric

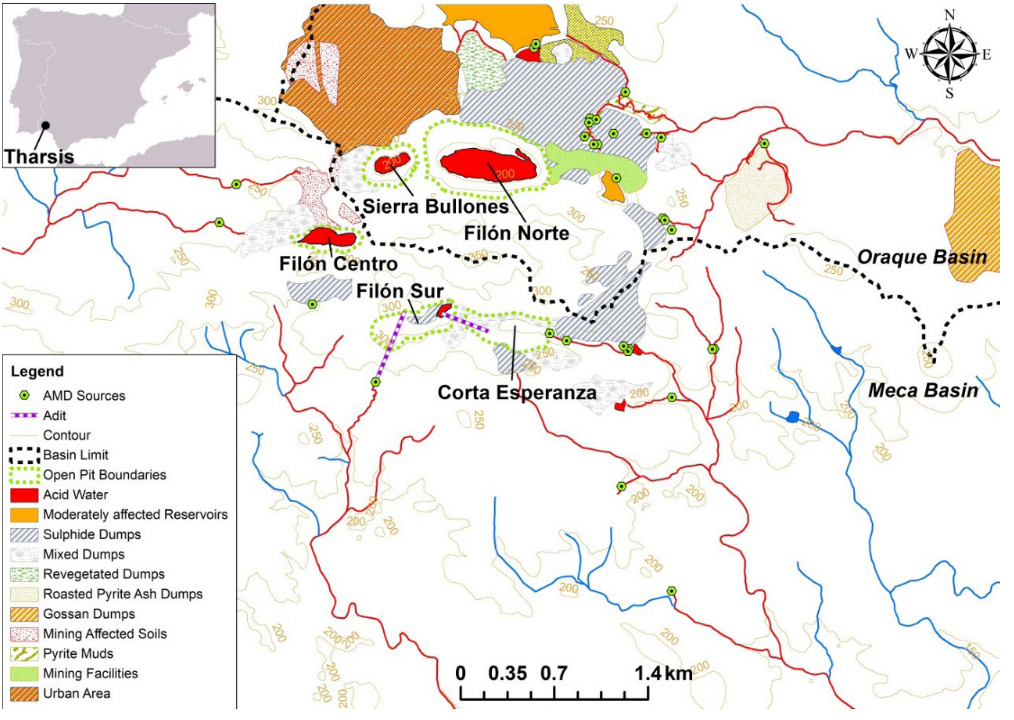

Figure 1 Map of the Tharsis mining district showing the affected streams and the main AMD sources.

oxygen. These acidic waters end up in the streams of the area causing their pollution. The main goal of this paper is to show a global perspective of the serious problems that exist in this zone, after the total cessation of mining activity in 2001 and propose some lines of action to improve the situation.

Methods

A cartography of the surface affected by mining has been made, classifying dumps based on pollutant potential. Two samplings in different hydrological conditions (dry and wet periods) were carried out in the mining area to collect acidic leachates from the main AMD sources. When possible, the discharge of the sources were measured with a current meter. Two small reservoirs located in the mining area and the flooded open pits (Fig. 1) have also been sampled. Samples were filtrated through 0.45 µm Millipore Teflon filters, acidified with HNO_3 suprapur to pH<2, and kept in the dark at around 4°C until analysis. Temperature, electrical conductivity (EC), redox potential and pH were determined in the field with portable meters. The instruments were calibrated and checked against certified standards. Analyses were performed using ICP-OES and ICP-MS. Different elements were determined but here only Al, Cu, Fe, Mn, Zn, As, Cd, Co, Pb and sulfate will be shown.

Results

There is an area of 3.94 km^2 affected by mining, mainly covered by spoil heaps (2.44 km^2), open pits (0.85 km^2) and mine soils (0.54 km^2). The dumps have been classified into 5 different types:

1. Spoil heaps composed mainly of sulphides (Fig. 2), the most important being to the northeast of Filón Norte and to the east of Corta Esperanza (Fig.1). They are very large, with altitudes of up to 80 m, and produce the higher loads of acidic waters.
2. Mixed dumps with different types of materials, including sulphides. They are smaller in size and also have less polluting potential due to their lower sulphide content.
3. Dumps of roasted pyrite ashes, wastes coming back from factories where the

Figure 2 *Left: Picture of the top of a large sulphide-rich dump (notice the sinkholes caused by sulphide dissolution). Right: large amounts of evaporitc salts at the base of sulphide-rich dumps (end of the summer).*

ore was transported for the extraction of sulphuric acid. These dumps have some isolation measures and generate relatively few acid leachates.

4. Gossan heap leaching wastes from the treatment of gossan by cyanide to obtain gold and silver. They are located to the east of the mining area and do not produce substantial acid leachates.
5. Revegetated spoil heaps, located to the east of the urban area. Its original topography has been remodelled to give them a more natural appearance and has been covered with soils that allows the growth of vegetation. Visually these areas are in good condition. However, there are no isolation measures to prevent the infiltration of rainwater and the influx of atmospheric oxygen, so that some AMD sources exist (Fig. 1).

Besides that, in the area there are 5 open pits, one of which is filled by mining wastes (Corta Esperanza, Fig. 1). The other 4 are partially flooded with acidic waters with high concentrations of metals and metalloids (Sánchez España et al. 2008). The water level in the Filón Centro and Filón Sur pit lakes is stabilized, while in Filón Norte and Sierra Bullones, connected by underground galleries, is rising at an average rate of 2.8 m/year (Moreno González et al. 2018). The volume of stored acidic water was 5.2 hm^3 in 2016, most of it (3.6 hm^3) is found in Filón Norte. In total, the dissolved metals in the pit lakes are close to 9000 t of Fe, 1000 t of Al and Zn, etc. (Moreno González et al. 2018). On the other hand, in the mining area there are also two shallow reservoirs that are slightly affected by acid leachates and have pH values between 4 and 5. The largest is the one located to the north, with a surface area of 0.27 km^2 (Fig. 1).

There are about 30 AMD sources which cause the severe pollution of surrounding streams (Fig. 1), although some are temporal and dry out during the summer. Table 1 summarizes the values obtained from the samplings. Flow rates ranged from less than 0.1 to 13 L/s in the wet season, while in the dry season the maximum flow rate was 2.5 L/s. The average pH values are close to 2.5, with some values close to zero or even negative (-0.2). The EC values are between 1 and 70 mS/cm, with mean values between 12 and 14 mS/cm and median between 6 and 9 mS/cm. The concentrations of metals and metalloids are also very high, with maximum values of 194 g/L of Fe, 11 g/L of Zn, 8 g/L of Al and 2.3 g/L of As. These extreme values are reached in seepages from dumps composed almost exclusively of sulphides, which give rise to precipitates with spectacular melanterite crystals. More representative are the median data, with values of 668 - 412 mg/L for Fe (dry and wet samplings), 494 - 369 mg/L for Al and 0.3 - 1.3 mg/L for As (Table 1). Median concentrations are higher in the dry period sampling except for As and Pb, which have higher values in the wet sampling.

During periods without rainfalls, especially during the summer, the evaporation of acid waters with high concentrations of metals and sulfate produces the precipitation

Table 1 Statistical summary of flow rates, pH, EC and dissolved concentrations for the two samplings

	Q	pH	EC	Al	Cu	Fe	Mn	Zn	As	Cd	Co	Pb
	L/s		mS/cm					mg/L				
						Dry Period (n=18)						
Min.	<0.1	0.35	1.4	7.9	1.0	3.6	2.1	4.3	0.004	0.01	0.20	0.02
Max.	2.5	3.36	35.2	8180	2410	102640	1290	11180	1164	12	28	2.8
Mean	0.5	2.59	12.0	1164	215	7477	146	828	72	1.1	8.0	0.33
Median	0.1	2.71	8.7	494	80	668	50	82	0.3	0.2	4.2	0.06
Std. Dev	0.8	0.67	10.4	1983	557	23905	302	2608	281	2.9	8.4	0.73
						Wet Period (n=29)						
Min	0.1	0.20	1.0	18	0.8	15	2.2	3.3	0.003	0.004	0.14	0.01
Max	13.4	3.87	70.6	6138	3511	194220	922	10910	2258	11	46	14
Mean	4.3	2.29	13.7	944	330	17267	117	964	183	1.2	7.6	1.0
Median	3.1	2.40	6.4	369	61	412	47	53	1.3	0.14	2.8	0.12
Std. Dev.	3.7	0.75	17.0	1503	794	48721	216	2477	575	2.8	11	3.1

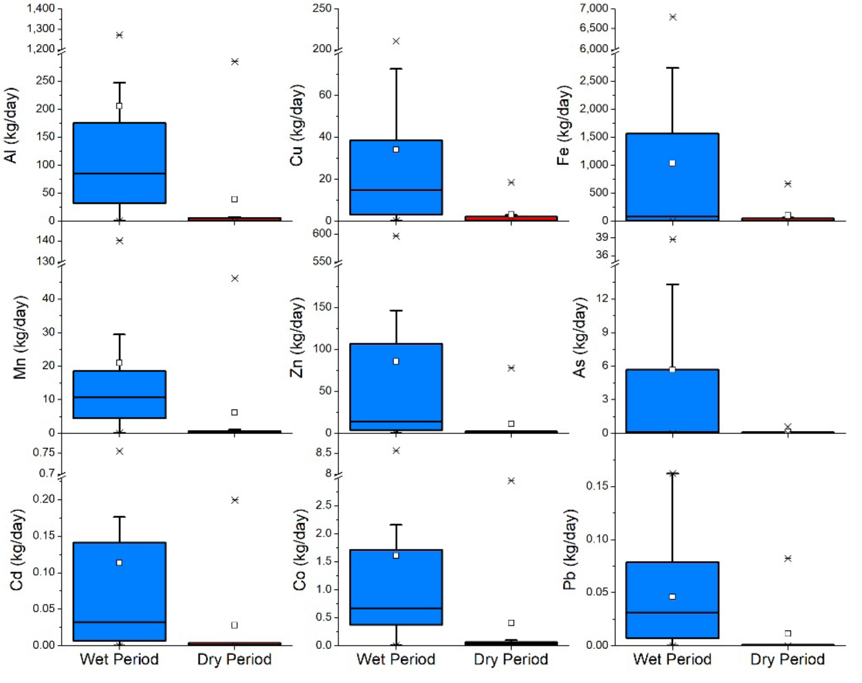

***Figure 3** Box-plot diagrams for the contaminant load of each sampling.*

of large amounts of evaporative salts throughout the mining area (Fig. 2) and on the margins of the affected courses (Valente et al. 2013). These salts are washed quickly with rainfalls following a prolonged dry period, causing a large increase in the concentration of metals and metalloids in the water.

Figure 3 summarizes the pollutant loads released by the AMD sources. The highest loads are found in winter, when flows are much higher. The amount of pollutants released by some of these sources is extreme (e.g. up to 6.8 t/day of Fe, 1.3 t/day of Al and 39 kg/day of As). The median values, although notably lower, are also very high for the wet period sampling.

The largest pollutant loads come from the large sulphide-rich dumps located to the east of Corta Esperanza and, especially, to the northeast of Filón Norte (Fig. 1). These contributions have a profound effect on the Aguas Agrias creek, which flows westwards into the Oraque River, which also receives pollutants from other mines located in its basin (Olías et al. 2011). On the other hand, acid leachates from AMD sources in the south and west of the area flow southwards through several streams and join the Meca river (Cánovas et al., 2017). As a result, 115 km of watercourses are heavily polluted, in most cases with pH values of less than 3 and high concentrations of metals and metalloids.

The Meca river is regulated by the Sancho reservoir, the largest in the Odiel basin with a capacity of 58 hm^3. Due to the acid contributions received, the water stored in this reservoir has a pH close to 3.5 and substantial concentrations of toxic elements (e.g. 4.4 mg/L of Al and 1.9 mg/L of Zn). In addition, there is a trend of worsening attributed to the rebound effect after the mine closure in 2001 (Cánovas et al. 2016). There is a great interest for using this water for irrigation, but the necessity to build a neutralization plant and its high maintance cost compromise its feasibility.

Downstream of the confluence between the Oraque and Odiel Rivers, a new reservoir of 246 hm^3 of capacity is being built. Both the Oraque and Odiel rivers are heavily contaminated by AMD. According to the reservoir project, the water will have a neutral pH and good quality. However, according to estimates by Olías et al. (2011), if measures are not taken to eliminate the main sources of acidic waters, the reservoir will have conditions similar to or worse than those of the Sancho reservoir.

The acidic waters of the Tharsis mines finally flow into the Odiel River, also contaminated by other mines, which in turn flows into the estuary of the Huelva Estuary. The estuary receives a large quantity of metals and metaloids transported by the rivers Tinto and Odiel, consequently producing an important contamination in this coastal system (Nieto et al., 2007).

In summary, the Tharsis mines constitute one of the most polluting in the IPB, producing a total degradation of the Aguas Agria creek, a tributary of the Oraque river, and of numerous streams of the Meca river basin, and contribute to the important contamination by metals and metalloids of the estuary of the Ría de Huelva. In addition, acidic waters compromises the possibility of using the water of the reservoirs in the area. Consequently, actions are urgently needed to improve conditions and to reduce the levels of pollutants emitted.

The very high concentrations of metals in the Tharsis AMD sources mean that the passive treatment methods usually used to treat AMD (wetlands, anoxic limestone drains, reducing systems and alkalinity producers, etc.) cannot be applied. For these waters, with extreme concentrations of Fe, Al and other metals, the DAS –Dispersed Alkaline Substrate- technology has been developed (Ayora et al. 2013). This method is based on passing the acidic water through ractive tanks filled with a mixture of: 1) fine grained limestone, in order to obtain a high specific surface area and avoid the passivation by a layer of iron precipitates, and 2) an inert material (wood shavings) to give a high porosity and permeability to the system, to avoid clogging problems due to the precipitation of the large quantity of metals contained in the acidic waters (Ayora et al. 2013). The accumulation of rare earth elements and yttrium (REY), elements of high technological and strategic interest in a specific part of the reactive tank when pH values are close to 5, could contribute to financing, at least partially, the maintenance costs of DAS plants (Ayora et al. 2016).

This technology is being successfully used in two passive treatment plants built at the Esperanza and Concepción mines, also located in the Odiel basin. However, the high flow values together with the high concentrations of metals from the AMD sources of the Tharsis mines would require the construction of huge reagent tanks or frequent replacement of the limestone-wood shaving mixture. It would be therefore necessary to combine the construction of DAS plants with the isolation of the most sulphide-rich tailings to reduce the amounts of acidic waters generated. Another possibility would be the construction of an active neutralisation plant, but this option does not seem viable due to its high maintenance costs, which would have to be paid indefinitely.

Conclusions

The extractive activity in the Tharsis mines ceased completely in 2001, but the acidic waters generated by the waste generated during 140 years of mining continue to pose a serious environmental and socio-economic problem in the area. The affected surface is close to 400 ha. Different types of spoil heaps have been differentiated, the ones with the greatest polluting potential are those that are fundamentally constituted by sulphides, some of which are up to 80 m high. There are around 30 main sources of acid mine drainage with discharges between 0.1 and 13 L/s, pH values lower than 3, electrical conductivity values ranging from 1.0 to 71 mS/cm and high concentrations of Fe (up to 194 g/L), Al (up to 8.1 g/L), As (up to 2.2 g/L), etc. The load of pollutants released from the mining area varies depending on the rainfall regime, reaching values in some sources of up to 6.8 ton/day of Fe, 1.3 ton/day of Al, etc. In addition, in the area there are 4 flooded open pit, with a volume of acidic water close to 5.2 hm^3. The water level in two of these pit lakes has not yet stabilized and continues to rise.

The acid leachates generated produce the degradation of 115 km of water courses of the Meca and Oraque Rivers, both belonging to the Odiel River basin. In addition, the Meca River basin is regulated by the Sancho reservoir (capacity of 58 hm^3), which has a pH close to 3.5 and substantial concentrations of toxic elements, so the water must be treated before being used for the supply to an industrial facility. Other acidic leachates join the Oraque River, where downstream the confluence with the Odiel River a new reservoir (capacity of 246 hm^3) is currently under construction. However, this reservoir will store acidic waters if remediation measures are not taken. Finally, acidic leachates from the Tharsis mines also contribute to the important pollution of the Ría of Huelva estuary.

A strategy based on the isolation of the most pollutant spoil heaps combined with the construction of DAS-passive treatment plants is proposed for the reduction of contaminant emissions from Tharsis and the improvement of the surrounding water bodies.

Acknowledgements

This work was funded by the Ministry of Economy and Competitivy of Spain through the SCYRE project (CGL2016-78783-C2-1-R).

References

Ayora C, Caraballo MA, Macías F, Rötting T, Carrera J, Nieto JM (2013) Acid mine drainage in the Iberian Pyrite Belt: 2. Lessons learned from recent passive remediation experiences. Environmental Science and Pollution Research 20(11):7837-7853, doi.org/10.1007/s11356-013-1479-2

Ayora C, Macías F, Torres E, Lozano A, Carrero S, Nieto JM, Pérez-López R, Fernández-Martínez A, Castillo-Michel H, (2016) Recovery of Rare Earth Elements and Yttrium from Passive-Remediation Systems of Acid Mine Drainage. Environ Sci Technol 50: 8255-8262, doi.org/10.1021/acs.est.6b02084

Cánovas CR, Olías M, Macias F, Torres E, San Miguel EG, Galván L, Ayora C, Nieto JM (2016). Water acidification trends in a reservoir of the Iberian Pyrite Belt (SW Spain). Sci Total Environ 541:400-411, doi.org/10.1016/j.scitotenv.2015.09.070

Cánovas CR, Macías F, Olías M, Pérez-López R, Nieto JM (2017) Metal-fluxes characterization at a catchment scale: study of mixing processes and end-member analysis in the Meca River watershed (SW Spain). J Hydrol, 550: 590-602, doi.org/10.1016/j.jhydrol.2017.05.037

Moreno González R, Olías M, Macías F, Cánovas CR, Fernández de Villarán, R (2018) Hydrological characterization and prediction of flood levels of acidic pit lakes in the Tharsis mines, Iberian Pyrite Belt. J Hydrology 566:807-817, doi.org/10.1016/j.jhydrol.2018.09.046

Nieto JM, Sarmiento AM, Olías M, Cánovas CR, Riba I, Kalman J, Delvalls, TA (2007) Acid mine drainage pollution in the Tinto and Odiel rivers (Iberian Pyrite Belt, SW Spain) and bioavailability of the transported metals to the Huelva Estuary. Environment International 33:

445-455, doi.org/10.1016/j.envint.2006.11.010

Olías M, Nieto JM, Sarmiento AM, Cánovas CR, Galván L (2011) Water Quality in the Future Alcolea Reservoir (Odiel River, SW Spain): A Clear Example of the Inappropriate Management of Water Resources in Spain. Water Resour Manage 25:201–215, doi.org/10.1007/s11269-010-9695-8

Sánchez España J, López-Pamo E, Santofimia E, Diez M (2008). The acidic mine pit lakes of the Iberian Pyrite Belt: An approach to their physical limnology and hydrogeochemistry. Appl Geochem 23: 1260-1287, doi.org/10.1016/j.apgeochem.2007.12.036

Tornos F, Lopez-Pamo E, Sánchez España FJ (2009) The Iberian Pyrite Belt. In: Agueda J, Palacios J, Salvador CI (Eds), Spanish Geological Framework and Geosites, IGME, p 56-64

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). App Geochem 39: 11-25, doi.org/10.1016/j.apgeochem.2013.09.014