Water resources degradation by acid mine drainage: the Sancho Reservoir (Odiel River Basin, SW Spain)

Manuel Olías[1], Carlos R. Cánovas[1], Francisco Macías[1], José Miguel Nieto[1]

[1]*Department of Earth Sciences, University of Huelva, Campus 'El Carmen' s/n 21071 Huelva, Spain, manuel.olias@dgyp.uhu.es*

Abstract The Sancho reservoir (58 hm³ of storage capacity) in the Odiel River Basin is an extreme case of AMD pollution. The reservoir receives acid leachates from the Tharsis mines, provoking low pH values and high dissolved metal concentrations. Although mining ended in 2001, a progressive worsening of the reservoir water quality has been detected since 2007. This seems to be linked to the uncontrolled dumping of milled pyrite wastes from nearby industrial facilities. Changes in AMD pollution levels in the main river feeding the reservoir were not apparent due to its high hydrological and hydrochemical variability, typical of the Mediterranean rivers. The monitoring of receiving water bodies, such as reservoirs, allows a more reliable detection of trends in water quality.

Key words Iberian Pyrite Belt, sulphides, water pollution, metals

Introduction

The Sancho reservoir is fed by the Meca River, a tributary of the Odiel River (Fig. 1). Both rivers are located in the Iberian Pyrite Belt (IPB), which hosts one of the largest concentrations of massive sulfide deposits in the world. The intense mining of these resources has left an immense amount of abandoned mine wastes in the area. The oxidation of sulphides contained in these wastes releases high loads of sulfate, acidity and metals, generating acid mine drainage (AMD) which provokes a strong deterioration of the water courses in the region (Sarmiento et al. 2009). Until now, this reservoir is the biggest of the Odiel basin, with a storage capacity of 58 hm³ and presents acidic conditions ($pH<5$) and significant dissolved metal concentrations (up to 4.4 mg/L of Al), which makes this reservoir an extreme case of surface water pollution worldwide. A new large reservoir with a capacity of 246 hm³ is currently under construction in the Odiel basin, although there is great concern about its final stored water quality (Olías et al. 2011). Although mining in the zone ended in 2001, a progressive worsening of the Sancho reservoir water quality has been detected in the last years (Cánovas et al., 2016). Here, we present the evolution of the water quality in the reservoir from 1994 to 2016, the latest data available.

Site description

The Sancho Reservoir was built in 1962 to supply water to a paper mill factory. The Meca River watershed has a surface of 315 km² with a maximum height of 394 m. The region has a Mediterranean climate, with mean rainfall close to 600 mm, but with high intra- and inter-annual variability (Galván et al. 2009). The average river flow is 0.84 m³/s and usually dries up during the dry season (from June to September). The river watershed is mainly underlain by IPB materials, with rocks belonging to the Phyllitic-Quartzitic (PQ) and Vulcano-Sedimentary Complex (CVS) groups. This latter outcrops at the northern area of the watershed and contains massive sulfide deposits forming the mining district of Tharsis, one of the largest of the IPB. The deposits are mainly composed by pyrite (more than 90%), followed by chalcopyrite, sphalerite, galena, chalcocite and covellite (Tornos et al., 1997).

These deposits were exploited by Tartessians and Romans but it is from 1853 when the mining underwent a great impulse for Cu extraction and, later, to obtain sulfuric acid. Also, the gossan has been exploited to obtain Au and Ag by cyanidation. Mining activity in Tharsis ceased completely in 2001 but there is an extensive area of flooded open-pits, galleries, shafts and mining wastes which release metal and acidity to the rivers. Therefore, the Meca River is currently deeply contaminated by AMD, transporting huge amounts of contaminants to the Sancho Reservoir (Galván et al. 2009; 2012). Most of these pollutants precipitate and are transferred to the bottom sediments (Sarmiento et al. 2009, Torres et al., 2014).

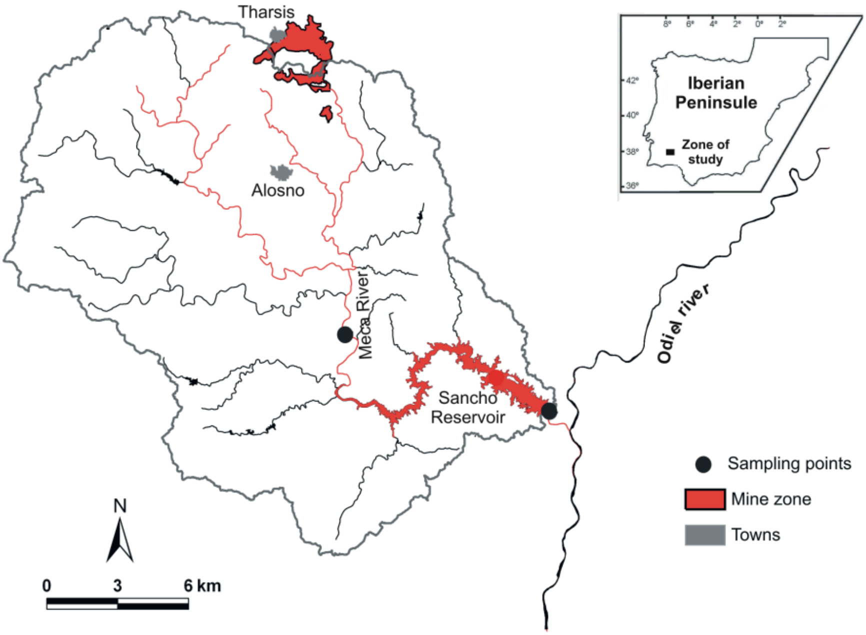

Figure 1 *Location map showing the streams affected by AMD.*

Methods

The Meca River hydrochemical information was obtained in a sampling point upstream the reservoir by several studies conducted since 2003 (189 samples). This includes analytical information from 2004 to 2006, 2009 to 2010 and 2012 to 2014 with a variable frequency (from monthly to daily). Most of the samples (114) correspond to a high-resolution sampling performed during the hydrologic year 2012/13. Hydrochemical data of the Sancho Reservoir was obtained from the Regional Water Authority, collected since 1994 to 2016 with around a quarterly sampling frequency, although there are years with one only sample. This dataset was completed with our own data from 2003/04 and 2008–2014 with a variable frequency. The samples were taken in the water surface from the top of the reservoir dam. Up to 103 measurements of electrical conductivity (EC) and pH are available for the reservoir data set (Table 1), with a lower number for sulfate (101), Zn (98), Cu (94), Mn (98), Fe (77) and al. (15). There are few analyses of the latter because it was not determined in the Water Authority controls.

The protocol for sample collection, handling and data quality assurance at laboratories was similar for both datasets. Samples were filtrated through 0.45 μm Millipore Teflon filters and acidified with HNO_3 suprapur to pH<2, and finally kept in the dark at around 4°C until analysis. Temperature, EC, and pH were determined in the field with portable meters. The instruments were calibrated against certified standards. Analyses were performed using ICP-OES. Different elements were determined but here only Al, Cu, Fe, Mn, Zn and sulfate will be used. Both laboratories have quality assurance and quality control protocols (Cánovas et al., 2016).

Results

During the study period reservoir waters showed pH values between 3.4 and 5.2, with an average of 4.3 (Table 1). The average EC was 0.42 mS/cm, with values ranging from 0.19 to 0.68 mS/cm. The highest mean concentrations of AMD-related metals were found for al. (4.4 mg/L), although the number of available samples for this element is low, followed by Mn (2.2 mg/L) and Zn (2.1 mg/L).

There are some oscillations in the evolution of pH values (Fig. 2). Nevertheless, it can be seen that pH values remained around 4.5 from 1994 to 2006, but a progressive decrease is observed since 2007, with values below 3.5 from 2014 onwards. In relation to EC, a slight upward trend seems to occur from 2000, which is more clearly defined since 2007. This tendency was interrupted at the beginning of 2010, coinciding with huge river inputs and a large rise of the water level in the reservoir (Cánovas et al., 2016). Other oscillations of EC values were subsequently observed related to rainfalls, remaining between 0.30 and 0.70 mS/cm.

Table 1 *Results obtained for the Sancho Reservoir (1994-2016).*

	pH	E.C. mS/cm	Al mg/L	Cu mg/L	Fe mg/L	Mn mg/L	Zn mg/L	SO_4 mg/L
Data no.	103	103	15	94	77	98	98	101
Mean	4.3	0.42	4.4	0.65	0.45	2.19	2.05	147
Min.	3.4	0.19	1.6	0.31	0.01	0.21	1.01	61
Max.	5.2	0.68	14.3	1.83	5.25	3.86	4.22	305
Stand. Dev.	0.5	0.12	2.9	0.26	0.71	0.80	0.75	51

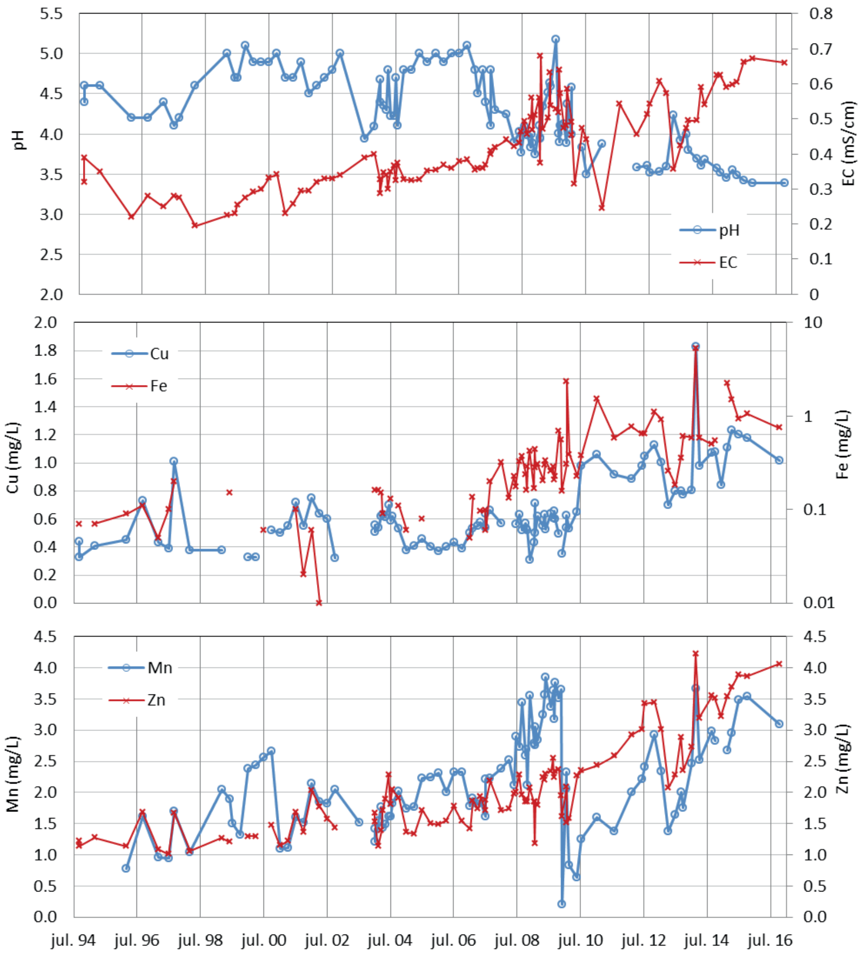

***Figure 2** Evolution of pH, EC and concentrations of some elements in the Sancho reservoir*

Sulfate concentration (not shown in Fig. 2) follows a similar evolution as EC, from 1994 to 2006 ranged from 70 to 150 mg/L while since 2007 values varied between 100 and 300 mg/L. The concentration of Fe in reservoir waters did not exceed 0.2 mg/L until 2007, being frequently even below the analytical detection limit. However, from this year onwards, a significant increase in concentration was observed, ranging usually between 0.2 and 1 mg/L and reaching up to 5.2 mg/L (Fig. 2). The concentration of Mn and Zn also began an upward tendency from 2007. Between 2007 and 2009 higher concentrations of Mn were found than for Zn, but from 2010 this tendency reverses. Manganese concentrations are affected by sharp decreases during the flood periods (Fig. 2). The concentration of Cu also shows a clear increase from 2010, later than the others, when pH values decrease below 4. With regards of the Meca River data upstream the reservoir, the mean pH and CE values are 3.1 and 1.57 mS/cm, respectively (Table 2). The most abundant toxic metal is al. (mean of 55 mg/L) followed by Fe, Zn, Mn and Cu (Table 1).

Table 2 *Results obtained for the Meca River (2003-2014).*

	pH	E.C. mS/cm	Al mg/L	Cu mg/L	Fe mg/L	Mn mg/L	Zn mg/L	SO_4 mg/L
Data no.	189	189	188	189	189	189	189	188
Mean	3.1	1.57	55	6.4	24	8.8	16	817
Min.	1.7	0.25	0.02	0.05	0.01	0.4	0.51	53
Max.	6.1	5.39	305	43	311	41	108	5440
Stand. Dev.	0.6	0.85	49	5.3	36	7.4	15	683

The available data show a high variability (Fig. 3). The evolution of pH and EC does not show a clear pattern or trend for the controlled period. Regarding concentrations, the higher values occurred in 2010 (the same that EC), just after a period of strong floods. The concentrations of Cu, Mn, Zn, al. and sulfates (the last two not shown in the figure) neither show a clear trend. On the contrary, Fe concentrations exhibited noticeably higher concentrations after 2007 (Fig. 3).

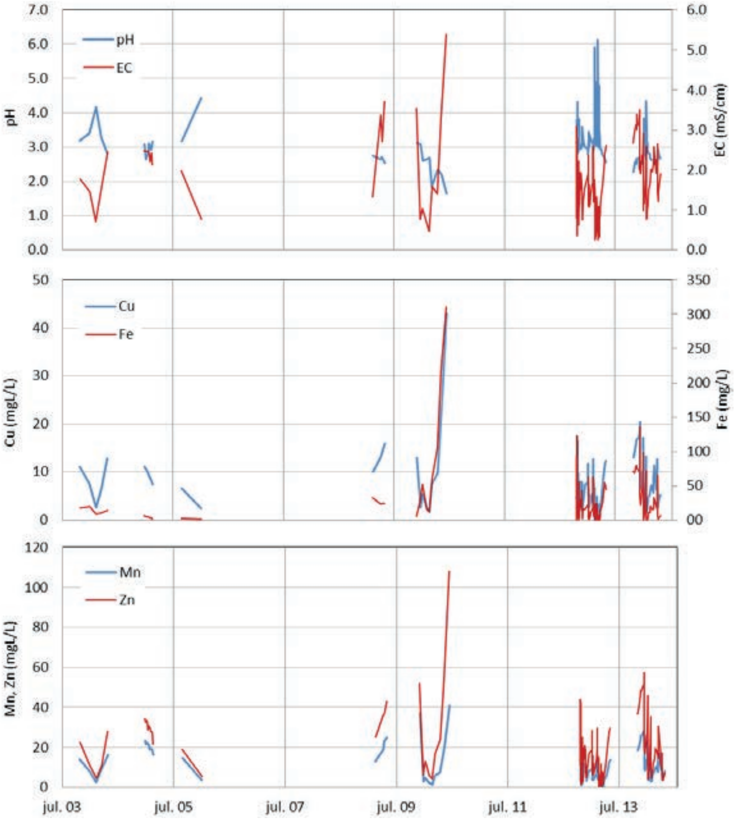

Figure 3 *Evolution of pH, EC and concentrations of some elements in the Meca River*

Discussion

The recurrence of dry and rainy periods causes oscillations of pH, EC and element concentrations in the river and, at to a lesser extent, in the reservoir (Figs. 2 and 3). In the IPB, the first rainfalls recorded in autumn provoke the wash-out of evaporitic soluble salts formed in the mining zones during summer, reaching the highest concentrations of sulfate and metals of the year (Cánovas et al., 2010). The opposite effect is observed during winter high floods, because of the dilution effect of runoff waters after all evaporitic salts have been washed. The occurrence of winter floods causes a decrease in EC values and metal concentrations in the reservoir by the dilution effect exerted by the high inputs of less mineralized waters, causing intra- and inter-annual hydrochemical variations in the reservoir. These variations are less noticeable in the Sancho Reservoir (Figs 2 and 3) because the effects are buffered when the river water mix with the reservoir stored water.

The reservoir is classified as holomictic with a turnover period lasting three months in winter. Seasonal hydrochemical variations occur in the hypolimnion related to the turnover and stratification periods. During stratification periods, when the conditions in the hypolimnion are anoxic, intense sulfate and Fe(III) reduction occurs in the first centimeters of sediment (Torres et al. 2013) increasing pH and Fe(II) concentration. During turnover, dissolved oxygen reaches the sediment surface and FeS previously formed in the shallower sediments is oxidized. However, Fe(II) is immediately oxidized and precipitated as schwertmannite. Consequently, pH and Fe(II) concentrations in the hypolimnion decrease in winter (Cánovas et al., 2016). Aluminum and other trace metals are also precipitated during stratification and are partially redissolved in winter. On the whole, there is a net flux of acidity and metals from the water column to the sediment (Torres et al, 2014). However, these changes barely affect the epilimnion, where samples were taken. On the other hand, during the summer evaporation at the epilimnion cause an increase in EC, sulfate and metal concentrations.

All these fluctuations are overlapped by a decreasing trend in pH values and an increase in EC and dissolved concentrations of AMD-related elements (Fig. 2), more clearly identifiable from 2007. This tendency must be linked to an increase of the pollutant load transported by the Meca River into the reservoir. The reason of the increase is not clear. These hydrochemical variations are not linked to shifts in the precipitation regime in the watershed but to the higher input of metals and acidity due to the rebound effect after the Tharsis mine closure in 2001 (Cánovas et al., 2016). Another cause that may have contributed to the increase of contaminants in the reservoir is the uncontrolled dumping of milled pyrite wastes from nearby industrial facilities in the Tharsis spoil heaps area. Remedial measures need to be adopted in AMD sources of the Tharsis mine in order to reduce the pressure on the water reservoir Apart from the change of Fe concentration before and after 2007 (Fig. 3), which could be easily unnoticed, the pollutant increment is not evident from the Meca River analyses. The high hydrologic and hydrochemical variability typical of the Mediterranean rivers can mask important changes in the pollutant load. The monitoring of receiving water bodies, such as reservoirs, where this variability is attenuated, allows a more reliable detection of long-term trends in water quality.

The differences in the evolution of the toxic metals elements in the reservoir are also influenced by their hydrochemical behavior. Thus, before 2007, Fe displayed very low concentrations, while al. was the predominant AMD-related metal buffering the water pH values between 4 and 5 (Fig. 2). At this pH range, Fe was removed from the solution by the precipitation of amorphous oxyhydroxisulfates. When the pH decreased below 4, the solubility of Fe increased. The increase of Cu concentration, which occurred in 2010 later that the Fe concentration rise, also seems controlled by some solubility control (Fig. 2). The observed decrease of pH values could change the transfer rates of pollutant between bottom sediments and water in the reservoir.

Conclusions

This work shows that the end of the environmental controls by the closure of Tharsis mine, together with the inadequate use of already polluted mining zones as industrial landfills, must be the main causes of the worsening of the Sancho reservoir water quality. Because of the high variability typical of Mediterranean rivers the increase of metal load transported by the Meca River is not evident while the monitoring of the reservoir clearly shows this trend. Thus, receiving water bodies such as reservoirs or lakes allows a more reliable detection of long-term trends in water quality. The evolution of toxic metal concentrations in the reservoir water shows some differences due to their different hydrochemical behavior. Remediation measures should be taken to reverse this trend and gradually improve the conditions of the Meca River and the Sancho reservoir.

Acknowledgements

This work was funded by the CGL2016-78783-C2-1-R and LIFE-ETAD ENV/ES/000250 projects.

References

Cánovas CR, Olías M, Nieto JM, Galván L (2010) Wash-out processes of evaporitic sulfate salts in the Tinto river: hydrogeochemical evolution and environmental impact. Appl Geochem 25:288–301, doi:10.1016/j.apgeochem.2009.11.014

Cánovas CR, Olias 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:10.1016/j.scitotenv.2015.09.070

Galván L, Olías M, Fernandez de Villarán R, Domingo Santos JM, Nieto JM, Sarmiento AM, Cánovas CR (2009) Application of the SWAT model to an AMD-affected river (Meca River, SW Spain). Estimation of transported pollutant load. J Hydrol 377:445–454, doi:10.1016/j.jhydrol.2009.09.002

Galván L, Olías M, Cánovas CR, Torres E, Ayora C, Nieto J.M, Sarmiento A.M (2012) Refining the estimation of metal loads dissolved in acid mine drainage by continuous monitoring of specific conductivity and water level. Appl Geochem 27:1932–1943, doi: 10.1016/j.apgeochem.2012.07.011

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 10.1007/s11269-010-9695-8

Sarmiento AM, Olías M, Nieto JM, Cánovas CR, Delgado J (2009b) Natural attenuation processes in two water reservoirs receiving acid mine drainage. Sci Total Environ 407:2051–2062, doi:10.1016/j.scitotenv.2008.11.011

Tornos F, Gonzalez Clavijo E, Spiro B (1997) The Filón Norte orebody, Tharsis, Iberian Pyrite Belt: a proximal low-temperature shale-hosted massive sulphide in a thin-skinned tectonic belt. Mineralium Deposita 33, 150–169

Torres E, Ayora C, Cánovas CR, García-Robledo E, Galván L., Sarmiento AM (2013) Metal cycling during sediment early diagenesis in a water reservoir affected by acid mine drainage. Sci. Total Environ 461/462, 416–429. doi: 10.1016/j.scitotenv.2013.05.014

Torres E, Ayora C, Jiménez-Arias JL, García-Robledo E, Papaspyrou S, Corzo A (2014) Benthic metal fluxes and sediment diagenesis in a water reservoir affected by acid mine drainage: A laboratory experiment and reactive transport modelling. Geochim et Cosmochim Acta 139:344-361. doi: 10.1016/j.gca.2014.04.013