Towards a Sustainable Restoration of a Watershed Strongly Polluted by Acid Mine Drainage (Amd); The Case of the Odiel River (Sw Spain)

Carlos Ruiz Cánovas[1], Jonatan Romero[1], Rafael León[1], Raúl Moreno-González[1], María Dolores Basallote[1], Francisco Macías[1], Rafael Pérez-López[1], Manuel Olías[1], Santiago García[2], José Miguel Nieto[1]

[1]*Earth Science Department and Research Center on Natural Resources, Health and the Environment (RENSMA). Huelva University, 21071, Huelva (Spain). carlos.ruiz@dgeo.uhu.es*

[2]*Department of Earth Sciences, Faculty of Marine and Environmental Sciences, University of Cádiz, 11510 Puerto Real, Spain.*

Abstract

The Odiel River is an extreme example of a watercourse intensively affected by acid mine drainage (AMD) due to historical mining in its catchment. The environmental regulations require the recovery of original conditions. However, a deep knowledge of metal loadings and the relative contribution of each AMD source is required to prioritize restoration measures in the catchment and assure the cost-effectiveness of the investment. Therefore, high-resolution sampling of the main AMD sources of the Odiel River was performed during high flow conditions and a geochemical model with the PHREEQC code was used to analyze the effect of restoration measures on selected areas of the catchment. The results obtained identified the Agrio River as the main pollutant contributor to the Odiel River. The modelling suggests that implementation of passive water treatment in low-flow AMD sources could contribute to the restoration of long lengths of currently polluted streams.

Keywords: Geochemical Modelling, Restoration Measures, Disperse Alkaline Substrate, Metal Pollution

Introduction

The Odiel River (SW Spain) is one of the main water courses draining the Iberian Pyrite Belt (IPB), with a drainage area of 2330 km^2 and a fluvial network of 1149 km but suffers from chronic AMD in 37% of the watershed due to historical mining activities. The Odiel River basin is mainly composed of three different sub-basins: Odiel basin, Oraque basin and Meca basin, all of which are affected by acid mine drainage (AMD) (Sarmiento et al., 2009). As a result, pH values below 4 and high concentrations of sulphate and metals characterize the main course of the river during the whole year. Owing to these extreme conditions, the Odiel River does not meet the requirements established by the European Water Framework Directive (WFD), and the deadline to reach a good water quality status in this water body has been extended until 2027. However, due to the severity and longevity of the AMD processes in the catchment, this achievement is currently unaffordable and urgent measures are needed. A deep knowledge of metal loadings and relative contribution of each AMD source is required to prioritize restoration measurements in the catchment and assure the cost-effectiveness of the investment. This is of paramount importance at mine sites characterized by diffuse sources with a complex response to variable hydrological conditions. This challenging situation is aggravated by the urgent need water for human consumption in this area, which led to the construction of a reservoir in the junction of the Odiel and Oraque rivers. The building of this water infrastructure was interrupted, but is now planned to continue despite serious doubts of the final water quality of the stored waters (Olías et al., 2011). Therefore, the main goals of this study were to determine the metal loadings and relative contribution of each AMD source and to build a geochemical model to predict the water quality and analyze the likely effectiveness of restoration measures on selected areas of the catchment.

Methods

A synoptic sampling during high flow conditions (January 2022) was performed in the Odiel River basin, collecting samples from the main AMD sources and streams. Samples were filtered through 0.45 μm and acidified to pH <2 with ultrapure nitric acid before chemical determinations. Different physico-chemical parameters such as pH, electrical conductivity (EC), redox potential (ORP) and temperature were measured in situ using a previously calibrated Crison MM40+ portable multimeter. Measured ORP values were referenced to the standard hydrogen electrode (Eh) according to Nordstrom and Wilde (1998). Two different devices were used for AMD-affected and -non-affected waters to avoid contamination of the probes. In the case of waters with pH > 4.5, alkalinity was also measured using Titrets kits. Then, samples were preserved at 4 °C before analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) for major elements and by inductively coupled plasma-mass spectroscopy (ICP-MS) for trace elements. The flow rates (Q) were estimated by determining the channel section and the velocity of water with a flowmeter (FP111 Global flow probe). The bucket method was used in the case of irregular channels and low discharge. Instantaneous metal loadings were estimated multiplying metal concentration at each point by its correspondent flow rate.

A geochemical model was also performed on data at high flow conditions using the PHREEQC code v3.14 (Parkhurst and Appelo, 2013) and the Wateq4f database enhanced with thermodynamic data for schwertmannite from Bigham et al. (1996). The model is based on successive mixing of tributaries across the catchment, using the MIX command that allows mixing two different aqueous solutions while fixing the mix ratios. For each mix, an equilibrium boundary is imposed based on experimental data. Thus, equilibrium with Fe and Al mineral phases (i.e. schwertmannite and basaluminite), typical of this environment (e.g, Sanchez-España et al., 2011) was established using the equilibrium_phases

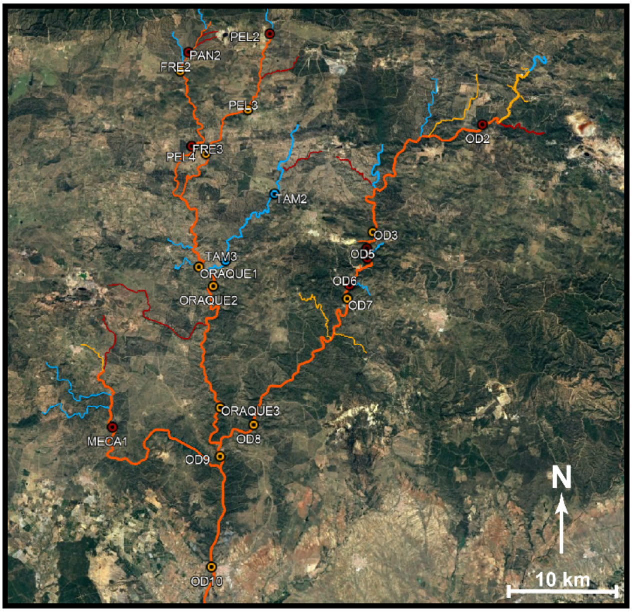

Figure 1 *Odiel River maps indicating the modeled confluence points. The colors indicate the affection degree of river courses (blue: not affected; yellow: slightly affected by AMD; orange: affected; red: severely affected).*

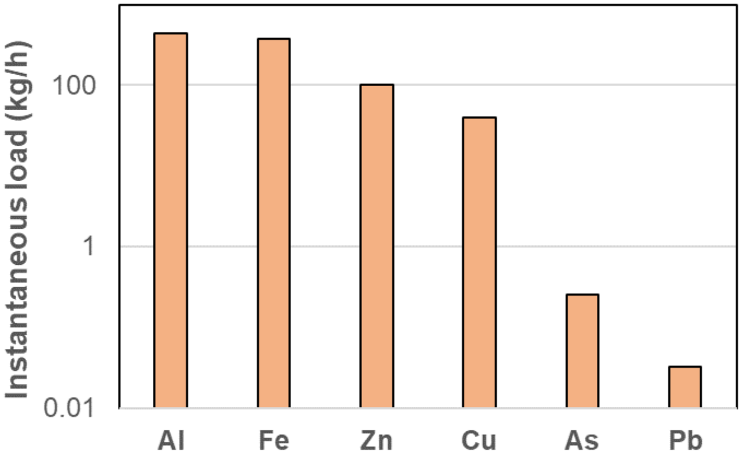

Figure 2 *Metal loadings from AMD sources to the Odiel River during the study period.*

command. This equilibrium was also extended to atmospheric gases in well-oxygenated waters. The different tributaries will be mixed downstream, achieving a general model of the watershed. For validation purposes, measured and modeled values for selected samples were compared. Once validated, a new model was built considering the partial (50%) or total reduction (100%) in pollution of the main AMD contributors of the Odiel River.

Results and Discussion

The results obtained during the study period indicate the high level of pollution of the Odiel River, with minimum values of pH along the watershed of 2.21 and metal concentrations of up to 3200 mg/L of Fe, 1540 mg/L of Al, 1160 mg/L of Zn, 179 mg/L of Cu, 4.4 mg/L of As, 1.74 mg/L of Cd or 0.47 mg/L of Pb. Although the year was not especially rainy, the high flows observed in the river led to the transport of high loads of metals to the Odiel River main course. For example, 122 kg/h of Al, 104 kg/h of Fe, 28 kg/h of Zn, 11 kg/h of Cu, 70 g/h of As and 8.0 g/h of Pb were transported from the main AMD sources to the river. Considering the main contributors to the river, the Agrio River, which deteriorate the Odiel river quality at OD2 (Fig. 1) stands out with the transport of around 63% of Cd, 60% of Al, 57% of Cu, and 46% of Zn. It is striking the low contribution of this AMD source with respect to Fe (25%), Pb (22%), and As (0.02%), which is related to the natural attenuation processes that cause the precipitation of Fe minerals and the co-precipitation and sorption of trace metals (Sánchez-España et al., 2011), while other more conservative elements remain in solution. It is worth noting that the sampling site is some km downstream of the Riotinto mining district, enhancing these natural processes. Other important metal contributors are the Aguas Agrias Creek and San Telmo mine transporting about 28% and 6% of the Fe, 17% and 1% of the As, 15% and 8% of the Zn, 10% and 6% of the Cu, 9% and 6% of the Al, and 12% and 6% of the Pb. The Meca River, which collect some of the AMD from the Tharsis mine, the second-most important in the IPB, constitutes another important source of pollutants to the river, contributing about 17% of the Zn, 13% of the Cu, 12% of the Pb, 22% of the Fe, 12% of the Al, and 58% of the As. However, in the case of the Meca River, most of these metals reach the Sancho Reservoir, where it may be trapped in the sediments (Cánovas et al. 2015). Therefore, from a practical point of view, it seems logical to focus the remediation actions to the Agrio River, Aguas Agrias Creek, and AMD from the San Telmo mine.

Regarding the geochemical model, comparing the modeled and measured values of Al and S (Fig. 3) revealed some deviations in those samples where the pH was > 4, where basaluminite precipitation starts. These differences, ranging from maximum values of

15% for Al and 40% for S, are attributed to the input of diffuse sources between sampling points and kinetic factors during the precipitation of basaluminite. The deviations observed for Fe are attributed to precipitation of . However, similar values were observed for modeled and measured concentrations for more conservative elements such as Mg, Na, and Cl.

Subsequently, the model was built assuming AMD abatement from the main AMD sources. In this sense, remediation of these AMD sources would lead to the improvement of the water quality, with a noticeable decrease in metal concentrations. A total reduction of AMD pollution from these sources would lower the concentrations of Fe, Al, and S would be reduced in around 98.6%, 99.8%, and 82.8%. On the other hand, the pH did not increase significantly (up to a value of 4.6), despite reducing the total load of metals from the main AMD contributors. This highlights the importance of the low-flow AMD sources, the net acidity of which may affect the water quality of the river. The remediation of these metal-rich and low-flow mining effluents can be approached by the settling of passive treatment systems, based on using a dispersed alkaline substrate (DAS), which has been successfully applied to metal-rich AMDs worldwide (Macías et al., 2017).

Conclusions

The Agrio River, which collects the AMD from the Riotinto mines, is the main metal contributor to the Odiel River, followed by the Aguas Agrias Creek and the San Telmo mine. According to the predictive geochemical model, even total remediation of these AMD sources would not cause good chemical water quality status in the Odiel River. Some other additional remediation of low-flow AMD sources must be applied. The implementation of passive treatment systems based on DAS technology has been effective in water quality amelioration worldwide, and could be an additional tool to recover the original conditions of the river. The starting of some of the IPB's largest mining operations could improve the environmental situation of the

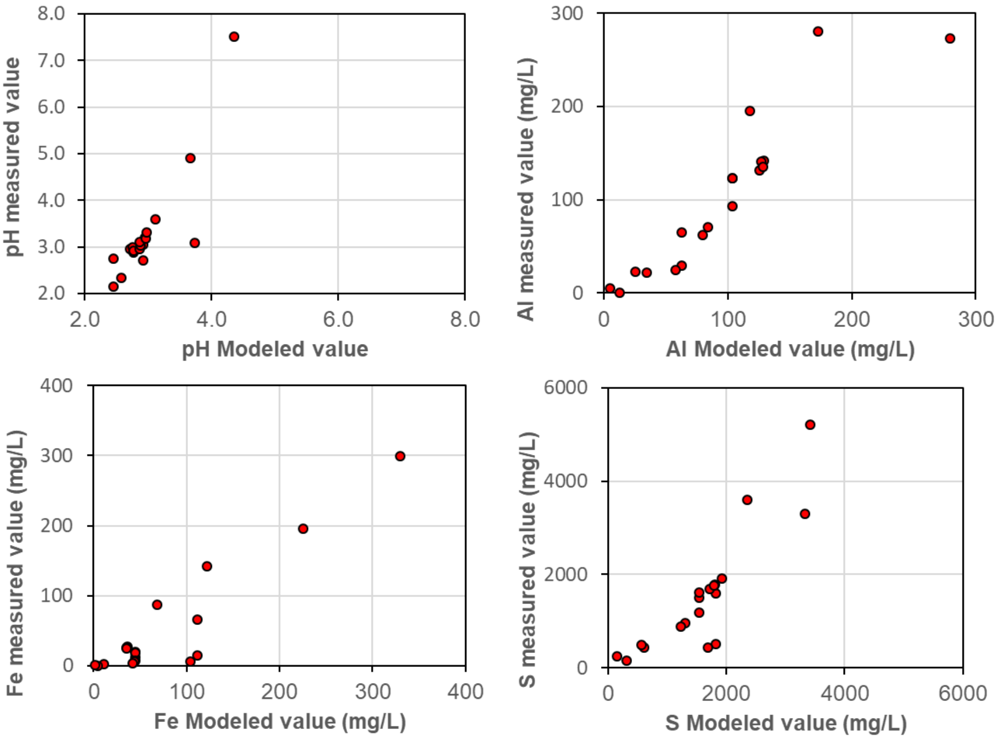

Figure 3 *Comparison between modeled and measured values in the study period.*

Odiel River watershed due to the assumption of past environmental liabilities by operating mining companies. The results obtained in this study will contribute notably to future restoration and help restore other catchments affected by mining worldwide.

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References

Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L., Wolf, M., 1996. Schwertmannite and the chemical modeling of iron in acid sulfate waters. Geochem. Cosmochim. Acta 60 (12), 2111-2121.

Cánovas, C.R., Olías, M., Macias, F., Torres, E., San Miguel, E.G., Galván. L., Ayora, C., Nieto, J.M, 2015. Water acidification trends in a reservoir of the Iberian Pyrite Belt (SW Spain). Science of The Total Environment 541, 400-411.

Macías, F., Pérez-López, R., Caraballo, M.A., Sarmiento, A.M., Cánovas, C.R., Nieto, J.M., Olías, M., Ayora, C., 2017. A geochemical approach to the restoration plans for the Odiel River basin (SW Spain), a watershed deeply polluted by acid mine drainage. Environ. Sci. Pollut. Res. 24, 4506-4516.

Nordstrom, D.K., Wilde, F.D., 1998. Reduction–oxidation potential (electrode method). National Field Manual for the Collection of Water Quality Data, Book 9, Chapter 6.5. U.S. Geological Survey Techniques of Water-Resources Investigations. U.S. Geological Survey, Reston, VA 20 pp.

Olías, M., Nieto, J.M., Sarmiento, A.M., Cánovas, C.R., 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 Resources Management, 25(1), 201–215.

Parkhurst, D.L., and Appelo, C.A.J., 2013, Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p.

Sánchez-España, J., Yusta, I., Diez-Ercilla, M., 2011. Schwertmannite and hydrobasaluminite: A re-evaluation of their solubility and control on the iron and aluminium concentration in acidic pit lakes. Applied Geochemistry, 26(9-10), 1752-1774.

Sarmiento, A.M., Nieto, J.M., Olías, M., Cánovas, C.R., 2009. Hydrochemical characteristics and seasonal influence on the pollution by acid mine drainage in the Odiel river Basin (SW Spain). Applied Geochemistry, 24(4), 697-714.