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TECHNICAL ARTICLE

A Statistical Determination of the Transit Speed of Pollutants in a Water Reservoir Affected by Acid Mine Drainage from the Iberian Pyrite Belt

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Abstract The El Sancho reservoir is located in the Odiel River basin, which crosses the Iberian Pyrite Belt. The reservoir receives acid mine drainage (AMD) from the Meca River, a tributary of the Odiel River. Two multi-parameter probes, one placed at the tail (up-gradient) end of the reservoir, where the contaminants enter, and another close to the reservoir dam were used to characterize acidity migration through the Sancho reservoir. The probes both measured pH and conductivity every 30 min. Two different levels of contamination were found, due to dilution that takes place within the reservoir and changes in the AMD composition. The cross-correlation function allowed quantification of the migration process from tail to dam. For both pH and conductivity, the maximum correlation occurred 17 days after sampling, indicating a mean transit time of 17 days. Since the distance between the two sampling points was 14,500 m, the contaminant transit speed was 0.0098 m/s.

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Keywords Water pollution · AMD · Mining dam · Iberian pyrite belt

Introduction

In any metallogenic province producing acid mine drainage (AMD), several surface media may be affected: water courses, open pits, estuaries, and mining dams. The temporal and spatial processes occurring in the first three media have been well described (Amils et al. 2011; Braungardt et al. 2003; Carro et al. 2011; Elbaz-Poulichet et al. 2001; Fernández-Remolar et al. 2005; Sanchez-España et al. 2005; Sainz et al. 2005; Santofimia and Lopez-Pamo 2013). In highly dynamic media, such as water courses and estuaries, physico-chemical parameters are controlled by factors such as water flow, hydrochemical inertia, input of non-polluted tributaries, tidal factors, and chemical composition of seawater. In contrast, mining dams and open pits represent more static media. Open pits, in most cases, are similar to an endorheic basin, in which the only water input comes from rainfall. When the piezometric level of the water table is higher than the depth of the pit, groundwater can enter the pit from infiltration or galleys, and can even inundate the pit.

In this study, we considered the El Sancho reservoir, a mining dam located in the Odiel River basin, which crosses the Iberian pyrite belt (IPB), one of the largest massive sulphide deposits in the world (Chopin and Alloway 2007; Kase et al. 1990). The IPB is about 230 km long and 30 km wide and is located in SW Europe. It extends from Seville in southern Spain to the western coast of Portugal, crossing the province of Huelva.

The Sancho reservoir is an extreme case of AMD pollution (Galvan et al. 2009) due to input from the Meca River, a tributary of the Odiel River (Fig. 1). The Meca

River receives polluted waters from different secondary tributaries affected by AMD, but mostly from the abandoned Tharsis mine, where waste dumps occupy an area of more than 300 ha, and there are two large open pits and several mining facilities (Valente et al. 2013). The Sancho reservoir is used for industrial purposes, to supply water to a pulp mill located 15 km downstream, in San Juan del Puerto (Grande et al. 2014).

Several authors have described the processes that affect the Sancho water reservoir: Sarmiento et al. (2009) described the natural attenuation there; Torres et al. (2013) discussed the reservoir geochemistry, and; de la Torre et al. (2014) modelled the hydrochemical changes that take place in the reservoir, at the confluence of a river polluted by AMD, as well as the possible attenuation of the pollutant load. Ceron et al. (2014) studied the relationship among physico-chemical variables, as well as hydrochemical variations associated with horizontal density induced stratification caused by vertical salinity and metals concentration variations.

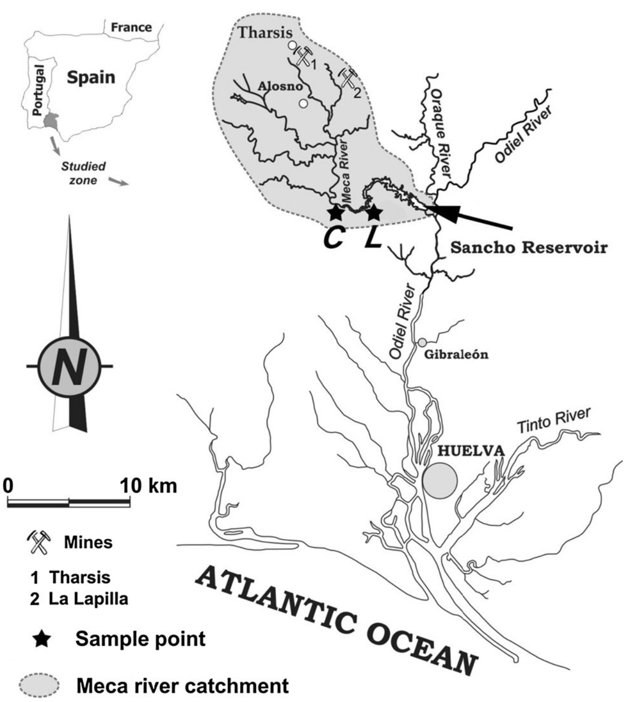


Fig. 1 Location map

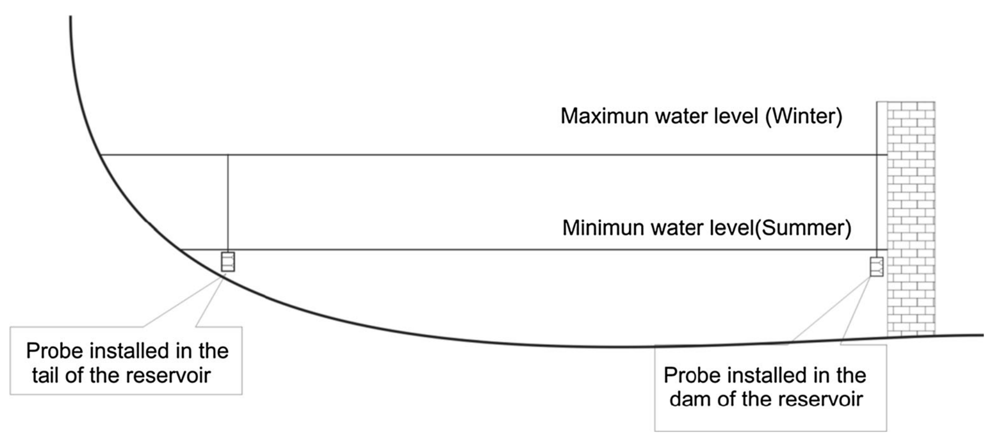
In the present study, we used a statistical treatment to characterize acidity migration in the Sancho reservoir. This methodology, based on Gray (1996) and Grande (2011), allowed us to estimate the transit speed of the pollution in the reservoir. The pH was selected as an indicator of the degree of the AMD impact in the reservoir. It is not feasible to use a single dispersion model for all dissolved metals, as the chemical composition of the water is manly controlled by pH. However, during the transit from the reservoir tail to the water main body, processes of hydrolysis, dissolution, precipitation, and even re-dissolution of previous metal precipitates occur. These processes depend on the flow rate of the AMD-affected stream and the size of the receiving reservoir. The tools and techniques used in this work to define the transit speed of pollutants are also suitable for studying other aquatic media affected by AMD elsewhere in the world.

Materials and Methods

Sampling Methodology

Two multi-parameter probes (Minisonde and MS5, Hydrolab) were placed at the El Sancho reservoir, one at the up-gradient (tail) of the reservoir and another close to the wall of the reservoir (Fig. 2), with a distance between them of 14,500 m. The probes allowed simultaneous pH and conductivity measurements every 30 min at both sampling points. The probes were maintained (cleaning of sensors, calibration, and battery replacement) weekly, and data were transferred to a laptop computer.

Fig. 2 Location of the two multi-parameter probes at the sampling points



The study period was from 1st October 2012 to 2nd April 2013, coinciding with the rainy season, which is when the Meca River, transports water loaded with AMD into the El Sancho reservoir. The study finished when the Meca River dried up. During the 183 days interval, the pH and conductivity were measured 8825 times.

Statistical Methods

After studying the statistical summary of variables, the data were statistically studied graphically for its autocorrelation and cross-correlation functions by means of the statistical package Statgraphics Centurion XV.II.

The autocorrelation function is suitable for cases in which one wishes to correlate the values for an ‘x’ variable at given times with those corresponding to an ‘x’ at previous times in order to know the system inertia. This function measures the existing correlation between the values taken by the variable for a ‘t’ instant and the ‘t + k’ instant, with ‘k’ being the delay or time passed between one observation and the following (Bisquerra 1989). Likewise, the cross-correlation function estimates the correlation that exists between a time series at a ‘t’ time and a second series at a ‘t + k’ instant as the function of delay or differential time ‘k’. It is particularly useful if two series are related to each other and, if they are, to determine whether one leads to the other. More details about these statistical methods may be found in de la Torre et al. (2011) and Grande et al. (2010c).

Results

Statistical Summary

Daily mean values were calculated for pH and conductivity and these means were used for the statistical treatment. Table 1 summarizes the basic statistical parameters of both variables. The mean conductivity values during the study period were significantly higher at the tail (750.8 µS/cm) than at the wall of the reservoir (599.5 µS/cm). The variability of the conductivity and the pH were 38 and 34 times higher at the tail than at the wall of the reservoir, respectively. Also, the mean pH was 0.2 higher at the tail than at the Wall, but since pH is a logarithmic scale, even relatively small changes in pH can be significant. Extreme

Table 1 Statistical summary

	Cond at dam (µS cm^{-1})	Cond at tail (µS cm^{-1})	pH at dam	pH at tail	Rainfall (mm)
Mean	599.5	750.8	4.0	4.2	40.2
Variance	2127.2	80761.5	0.0	1.1	7494.8
Minimum	562.5	267.7	3.7	2.7	0.0
Maximum	680.2	2427.3	4.3	7.6	450.0
Range	117.7	2159.5	0.6	4.8	450.0

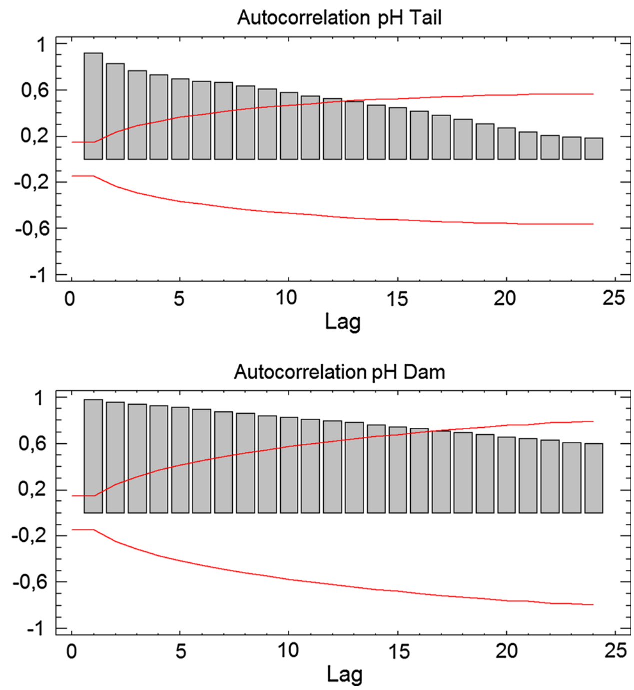


Fig. 3 Autocorrelation function for pH at the tail and the dam

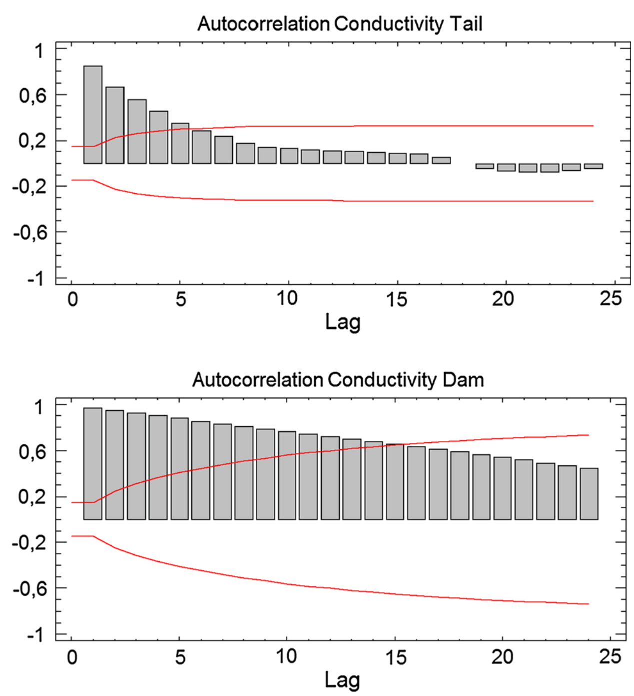


Fig. 4 Autocorrelation function for conductivity at the tail and the dam

maximum and minimum pH values were found at the tail (2.7 and 7.6) while the maximum and minimum dam pH values (3.7 and 4.3) were more stable. Also, the ranges of the conductivity and the pH at the tail were about 19 and 8 times larger than at the dam, respectively.

Autocorrelation Functions

Figures 3 and 4 show the results of applying the autocorrelation function to the mean daily conductivity and pH values at the two sampling points. It can be seen in Fig. 3 that there is a memory of 12 days for pH at the tail of the reservoir, corresponding to the cut-off point at $k = 12$. For the dam, the cut-off point shifts considerably to the right of the graph, reaching a value of k of 17 days. For conductivity (Fig. 4), this displacement is even greater; the memory is only 4 days at the tail, but 15 days at the dam, almost 4 times greater.

Cross-correlation Functions

The cross-correlation function (CCF) warns about the existence of significant correlation coefficients between the sampling points for pH (Fig. 5) and conductivity (Fig. 6). There were no remarkable turning points or strong trends in either graph, indicating consistent measurements, without outliers. Note that the maximum correlation phased out at 17 days for both conductivity and pH, so that CCF values peaked at that point.

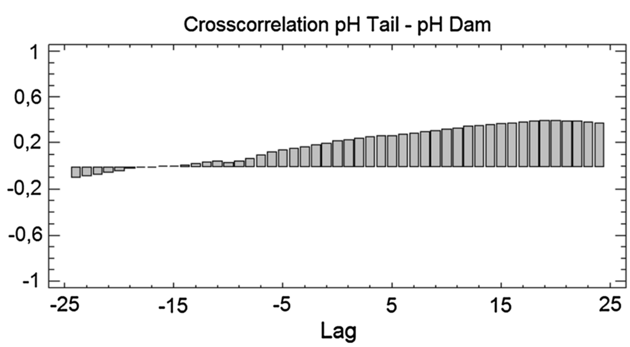


Fig. 5 Cross-correlation function for pH at the tail and the dam

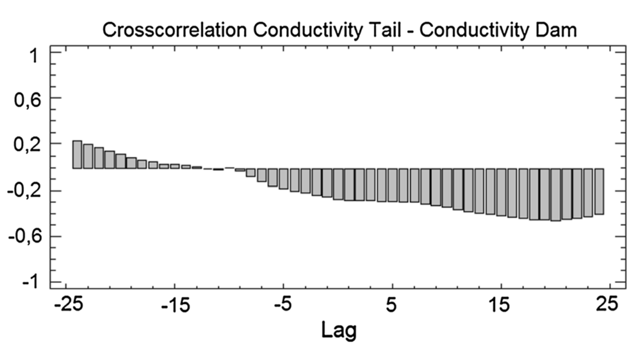


Fig. 6 Cross-correlation function for conductivity at the tail and the dam

Discussion and Conclusions

The basic statistical parameters in Table 1 are typical of water affected by AMD. The conspicuous differences at the two measuring points was are the result of dilution that takes place within the reservoir and changes in the input water quality. The variability of the chemical composition of Meca River depends on several factors, such as rainfall, the season of the year, and the leachates coming from waste rock dumps along its water course, as described by Sainz et al. (2002).

Higher mean conductivity values were always found at the tail of the reservoir than at the dam, due simply to dilution of the influent water as it enters the reservoir (Grande et al. 2010a). The neutral pH observed at the tail reflect periods of heavy rain.

Greater variability for both pH and conductivity was observed at the tail, reflecting the greater "hydrochemical inertia" (de la Torre et al. 2011; Grande et al. 2010b) in the reservoir due to the greater depth, greater distance from the pollution source, and the large water volume of the reservoir. Extreme acidity and conductivity values occur at the tails during the dry season, when the water input dominantly comes from the severely polluted mining areas. On the other hand, during the rainy season, the residence time in the waste rock dumps and thus leaching of AMD is less. During the floods that happen during the rainy season, the pH of the water increases (de la Torre et al. 2011).

The autocorrelation functions (ACF) for pH and conductivity corroborate the previous statements. The great differences in the "memory" of each series can be explained as follows: The autocorrelation function applied to the series studied shows the value for correlations between each variable on 1 day and the same variable on the previous days. This tool has been widely used for hydrochemical characterization (de la Torre et al. 2011, 2014; Grande et al. 2010c), which allows a numerical estimation of the resistance that a mass of water has to a change in its physicochemical characteristic to an external stimulus (Grande et al. 2010b). In this sense, the present results highlight the greater resistance at the dam than at the tail of the reservoir.

The cross-correlation function (CCF) allowed us to quantify the migration process. Thus, despite the fact that we are considering different numerical series, a common maximum was obtained for pH and conductivity, which allowed us to propose a dispersion wave transit time of 17 days from tail to dam. Variations happen, of course, depending on factors such as rainfall episodes and/or alteration of the chemical composition of the AMD input into the reservoir. The speed of the dispersion wave can be also estimated. As the mean transit time is 17 days, and the distance is 14,500 m, the wave speed is approximately 0.01 m/s.

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