Sediment Diagenesis Modelling in an AMD Contaminated Reservoir

/ E. TORRES (1,*), R.M. COUTURE (2), B. SHAFEI (3), C.R. CÁNOVAS (4), P. VAN CAPELLEN (2), C. AYORA (1)

(1) GHS, Instituto de Diagnóstico Ambiental y Estudios del Agua (IDÆA). CSIC. C/ Jordi Girona 11. 08028 Barcelona (España)
(2) Earth and Environmental Sciences, University of Waterloo, 200 University Ave. West, Waterloo, ON (Canada)
(3) School of Earth and Athmospheric Sciences, GA. Institute of Technology. 311 First Drive, Atlanta, Georgia, USA
(4) Department of Geodynamics. University of Huelva. Av. Fuerzas Armadas s/n. 21071 Huelva (Spain)

INTRODUCTION.

Acid mine drainage and associated metals are an environmental and ecological problem in many countries. In addition to this problem, most mining activities have been abandoned, so that there is no specific responsible to be blamed for pollution. Polluting discharges can remain for decades or even centuries, once the mining activity is over resulting in the pollution, and often the complete degradation, of fluvial ecosystems. In the Iberian Pyrite Belt (SW Spain) these problems arise with great intensity, due to the large deposits of sulphides which have been mined intensively (Sánchez-España et al., 2005). Nowadays, the Tinto and Odiel rivers alone discharge around 8 and 1.5% of the Zn and Cu contributed by rivers to the oceans (Olias et al, 2006).

Despite of the pollution of some tributaries and the main river, the Spanish Hydrological Plan considers the Odiel Basin as the main source of water resources in the province of Huelva (SW Spain), and a dam has been planned – the Alcolea dam (311 hm^3)– in the main river. In a Mediterranean region, with a very irregular distribution of precipitation along the year, it is expected that the reservoir will contribute to dilute pollution by retaining most of the dilute water during floods. Moreover, if life is developed, alkalinity supply due to organic matter oxidation will contribute to increase alkalinity. The role of organic matter accumulating on the bottom of the reservoir could also contribute to create a sulphate-reducing environment and the retention of metals. Despite its potential impact in water quality, there is no much detailed information on the effect of a water reservoir on the cycling of metals from an Acid Mine Drainage.
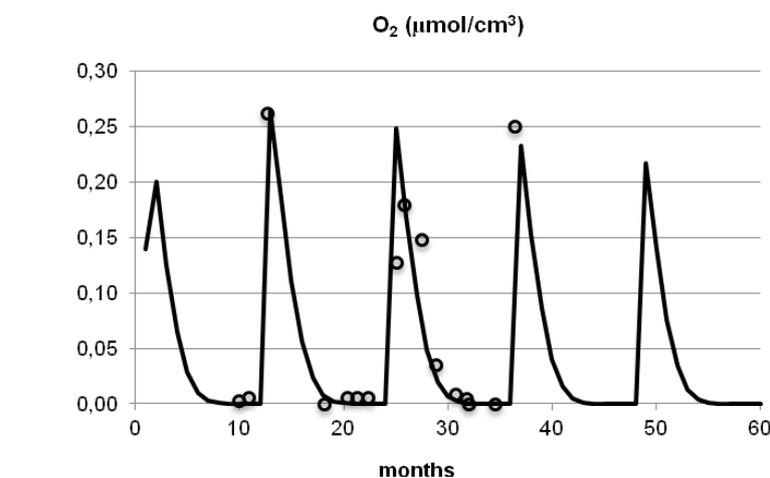

fig 1. Oxygen concentration in the upper part of the sediment versus time. The points correspond to analytical data and the line to the model results.

To better understand these processes we have selected a small reservoir located in the Odiel Basin which receives a strong impact of Acid Mine Drainage, and has become acidic along the years. We have studied the metal transfer between the water column and the sediment in order to estimate the metals bioavailability.

STUDY SITE.

The Sancho water reservoir is located in the Odiel Basin, Huelva (SW Spain) in the Iberian Pyrite Belt. The reservoir has a pH of ~4, with high SO_4 (200 ppm) and heavy metal concentrations in the water column. A monomictic behaviour forces the reservoir to mix in winter, and allow oxygen to reach the bottom. Solid and aqueous phases analyses show that the sediment acts as a sink of trace elements (e.g., As, Cd, Pb) during oxic conditions and as a source for them during anoxic conditions at the bottom.

METHODS.

Sample collection.

Field sampling was carried out from October 2008 to November 2010. Water sampling and in situ measurement of Eh, pH, temperature, O_2 (Fig. 1) were made in the water column. Several cores were taken along the reservoir in different seasons. Sediment was collected using cylindrical box corer (6 cm i.d). Each box core contains approximately 30 cm of sediment and 30 cm of overlying water. Some of the cores were immediately sectioned in a N_2 purged glove box in the laboratory and the others were frozen with liquid N_2, and sectioned after in a N_2 purged glove box.

Sample analysis.

To obtain the pore water, centrifugation tubes were transferred to a N_2 purged glove box, where the pore water was filtered through 0.2 μm pore size filters,

Fe(OH)₃ oxic conditions
(µmol/g)

Fe(OH)₃ anoxic conditions
(µmol/g)
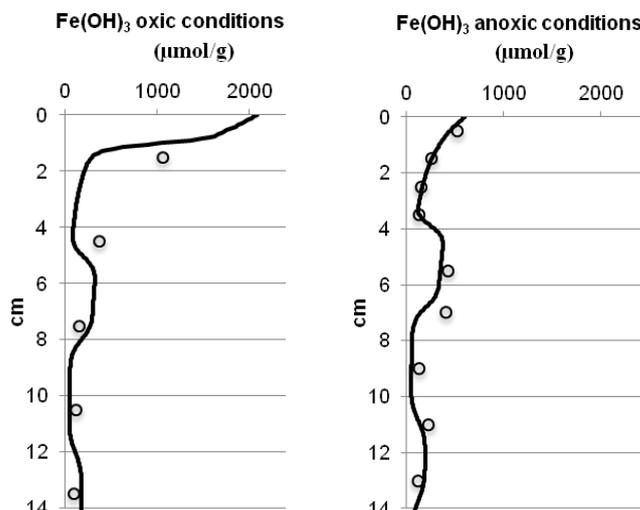
fig 2. Fe(III)-amorphous concentration in µmol/g under oxic (turnover, on the left) and anoxic (termocline, on the right) conditions versus depth (cm). The points correspond to analytical data and the line to the model results.

and pH, Eh and DO were measured. Sub samples for As, Co, Cu, Cd, Cr, Ni, Pb and Zn and for SO_4 and Fe were acidified with HNO_3 20% and stored at 4°C until analysis by ICP-MS and by ICP-OES, respectively.

Acid Volatile Sulphide (AVS), elemental sulphur (ES) and pyritic sulphur (PS) were determined by the method described in Van den Berg et al. (1998), with some modifications. Two different $Fe(OH)_{3(s)}$ pools (Fe (III)-amorphous and Fe(III)-oxides) were extracted with 0.2M oxalic acid at pH 3 at different temperatures (Dold, 2003). Organic matter fraction was extracted by 0.5M NaOH (Sposito, 1989).

MODEL FORMULATION.

Quantitative reactive transport model of sediment diagenesis has been performed by improving the apporoach outlined in Couture et al. (2010). The model has been modified by including: $FeCO_3$ as a new phase, pH and porosity functions with depth, and two organic matter (OM) pools. Due to the monomictic behaviour of the reservoir, non-steady-state boundary conditions were imposed as a function of time for O_2, as an error function, and for the $Fe(OH)_3(s)$ flux, because of its dependence on the O_2 concentration. The reaction network includes three primary reactions describing the degradation of organic matter via oxic respiration, Fe(III) and SO_4 reduction. The secondary reactions considered are the oxidation of pore water Fe(II) by O_2,

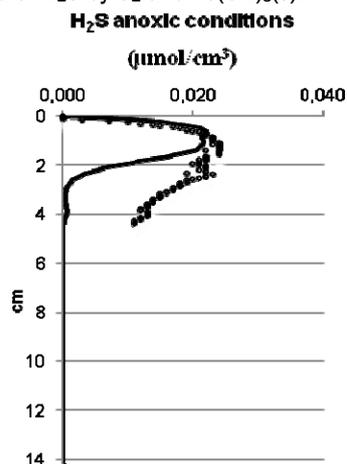and of H_2S by O_2 and $Fe(OH)_3(s)$.

H₂S anoxic conditions
(µmol/cm³)

fig 3. Sulphide concentration in µmol/cm³ under anoxic (termocline) conditions versus depth (cm). The points correspond to analytical data and the line to the model results.

RESULTS AND DISCUSSION.

SO_4 is completely reduced in the first few centimeters releasing H_2S (Fig. 3). Cadmium, Co, Cu Cr, Ni and Zn are diffused from the water column to the sediment. They are mainly adsorbed onto the organic matter in the upper part of the sediment profile and precipitated as sulfides.

Fe concentration in the solid phase decreases with depth as amorphous Fe(III)-hydroxide disappears. This is attributed to the dissolution of the Fe(III)- solid phase due to the stronger reductive conditions with depth. The Fe^{2+} is released to the pore water and tends to diffuse towards the water column and

precipitates as FeS near the interface where there is the H_2S generation. Arsenic is strongly linked to the Fe(III) minerals and its concentration in the solid phase decreases with depth while in pore water increases, due to Fe(III)-hydroxide dissolution, where As is a minor constituent.

The model predicts the fact that $Fe(OH)_3(s)$ and SO_4 are reduced in the upper few cm, releasing Fe^{2+} and H_2S which precipitate as FeS and pyrite. Excess of Fe^{2+} precipitates as $FeCO_3$. Under anoxic conditions solute concentrations on sediment pore water increase due to the absence of oxygen.

Owing to the time-dependent O_2 function implemented in the model (Fig. 1), we obtain a periodic response for the years simulated which allow us to reproduce the complex features of the measured sedimentary profiles (Fig. 2).

REFERENCES.

Couture, R.M., Shafei, B., Van Cappellen, P., Tessier, A., Gobeil, C. (2010): Application for arsenic diagenesis in the sediments of a perenially oxygenated lake. Env. Sc. Tech. 1, *44(1)*, 197-203.

Dold, B. (2003): Speciation of the most soluble phases in a sequential extraction procedure adapted for geochemical studies of copper sulfide mine waste. J. Geochem. Explor., *80*, 55-68.

Olías, M., Cerón, J.C., Moral, F. y Ruiz, F. (2006): Water quality of the Guadiamar river after the Aznalcóllar spill (SW Spain). Chemosphere, *62*, 213-225.

Sánchez España, J., López Pamo, E., Santofimia E., Aduvir, O., Reyes, J., Barettino, D. (2005): Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain). Geochemistry, mineralogy and environmental implications. Appl. Geochem., *20*, 1320-1356.

Sposito, G., Lund, L.J. y Chang, A.C. (1989): Trace Metal Chemistry in Arid Zone Field Soil amended with Sewage Sludge. I. Fractionation of Ni, Cu, Zn, Cd and Pb in Solid Phases. Soil Sci. Soc. Am. J., *46*, 260-264.

Van den Berg G.A. et al. (1998): Geochemical behaviour of trace metals in freshwater sediments. Environ. Toxicol. Chem., *17*, 758-763.