

Sediment-water elemental fluxes in a water reservoir affected by acid mine drainage

/ ESTHER TORRES (1), CARLOS AYORA (2), ALBERT NARDI (3), RAOUL COUTURE (4), BABAK SAFEI (5), PHILIPPE VAN CAPPELLEN (6)

(1) Department of Geodynamics and Paleontology, University of Huelva

(2) Department of Geosciences Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona

(3) Amphos21 Consulting SL, Barcelona

(4) Climate and Environmental Modelling, Norsk Institute for Vannforskning (NIVA), Oslo, Norway,

(5) Department of Earth and Atmospheric Sciences, Georgia Tech, USA

(6) Earth and Environmental Sciences, University of Waterloo, Canada

INTRODUCTION

Elevated concentrations of bioavailable metals in the sediments have a negative impact in biota and also affect the water quality. Therefore, an efficient management of lakes and water reservoirs requires of tools that enable us to understand their complex functioning and predict their behavior under changing conditions (pollutant discharges, remediation actions, climate change, etc.). In this study, we quantitatively evaluate the annual cycling of major elements and trace metals in a water reservoir affected by AMD under O_2 -oscillating concentrations using a reactive transport model.

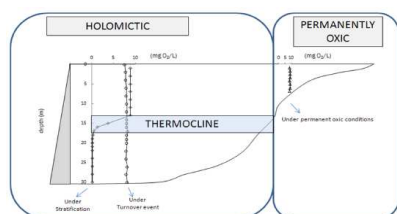


fig. 1. Section of the Sancho reservoir including the dissolved oxygen profiles of the holomictic and permanently oxic parts of the reservoir.

MATERIALS AND METHODS

The Sancho Reservoir (58 hm³) is located in the Odiel Basin in SW Spain. The reservoir has a surface area of 427 ha and a maximum depth of 40 m. The River Meca, the main tributary, is heavily contaminated by AMD with a mean pH of 2.6. The average stream flow is 61 hm³/year, most of which occurs during a few winter floods. During these floods, large amounts of particulate material are eroded from the river bed and transported into the reservoir. The reservoir was built in 1962, and the water was initially neutral, but is becoming acidic with time since Tharsis

mine closed in 1999 and water treatment ceased. The Sancho Reservoir has nowadays a pH of around 3.5. The reservoir is classified as holomictic with a turnover lasting two months during winter. During turnover, the entire water column is mixed, and dissolved oxygen reaches the sediment. During the rest of the year, the water column is stratified, and anoxic conditions are developed deeper than 15 m due to oxidation of the dissolved organic matter.

The study was based on three sediment core samples, two collected in the deep section of the reservoir during oxic (January 2010) and anoxic (October 2010) conditions, and one collected close to the river entrance (November 2010) under permanently oxic conditions (Figure 1). In order to estimate the annual solid fluxes (September 2009-2010), sediment traps were installed in the two reservoir sections. Water samples were also collected at the same points at three different depths.

Dissolved O_2 and H_2S , and pH in pore water were measured at millimetric scale using microelectrodes. The three

cores were divided into 1 to 2 cm-thick slices under N_2 atmosphere. The samples of the water column and the pore water, extracted of each slice by centrifugation, were analyzed by ICP-AES and ICP-MS. After freeze drying, the total composition including the organic carbon was obtained by Elemental Analyzer, and the mineralogy of the solid phases was investigated by X-ray diffraction (XRD) and Scanning Electron Microscopy and Microanalysis (SEM-EDS). A detailed sequential extraction procedure (Torres and Auleda, 2013) was applied to the solid phase. Details of the analytical methods and results are given in Torres et al. (2013). For space constraints of the abstract, only some results are plotted in Figure 2.

MODELING

The model formulation is based on a set of partial differential equations which directly couple transport (diffusion, bioirrigation and bioturbation) and reaction equations, following the sketch of Van Cappellen and Wang (1996). The reaction network is composed of 29 kinetic expressions. It includes four primary redox reactions describing the

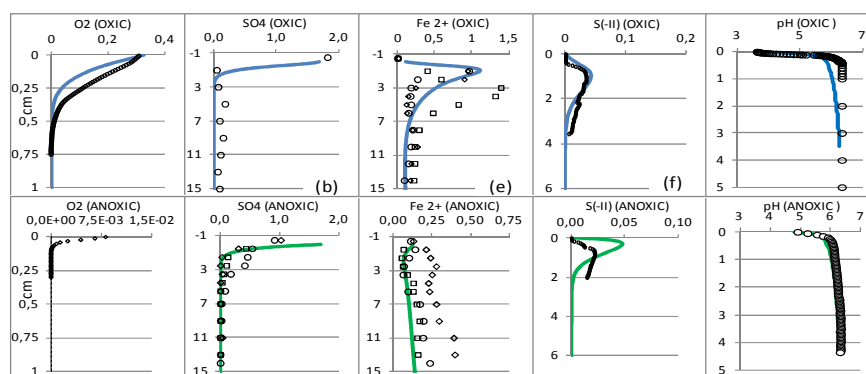


Fig.2. Calculated depth profiles of aqueous pore water concentrations ($\mu\text{mol}/\text{cm}^3$) at interannual steady state under O_2 oscillating conditions (holomictic). Points represent experimental data. Vertical scale in cm.

palabras clave: diagenesis, transporte reactivo, metales, nutrientes, cinetica redox, schwertmannita, oxidación de materia organica

key words: diagenesis, reactive transport, metals, nutrients, redox kinetics, shcwertmannite, organic matter oxidation

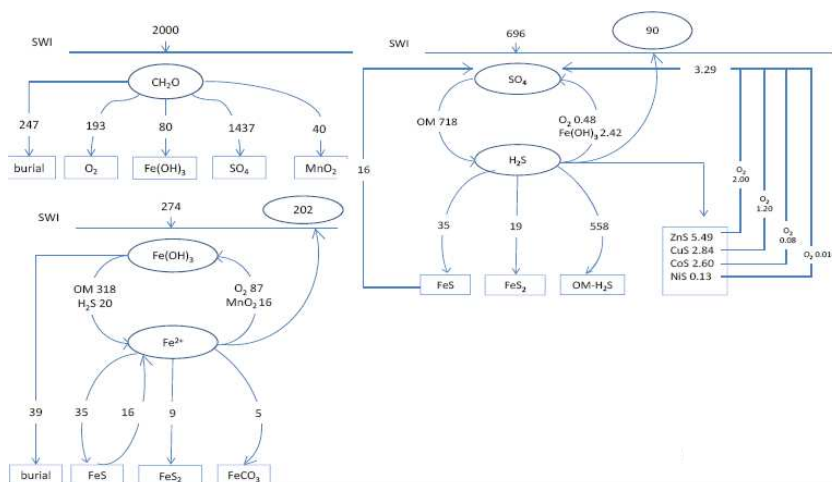


fig. 3. Depth integrated annual fluxes ($\mu\text{mol}/\text{cm}^2/\text{yr}$) in the upper 20 cm of the sediment column calculated under oxygen oscillating conditions (holomictic).

organic matter (OM) degradation via aerobic respiration, Mn-oxide, Fe-oxide and sulfate reduction. The secondary redox reactions considered were the Mn(II), Fe(II) and H_2S oxidation by O_2 , the oxidation of Fe(II) by Mn-oxide and the oxidation of H_2S by Fe-oxide. The dissolution-precipitation of the solid phases involved in the model was assumed proportional to the corresponding pore water saturation. Desorption of As from Fe-ox was linked to the Fe-oxide dissolution rate and to its stoichiometric As proportion. On the contrary, sorption reactions were treated as an irreversible process with a rate proportional to the sorbed solute and the solid sorbent. Fifteen aqueous species were used to calculate the aqueous speciation and saturation indices of the minerals.

The results of these analyses will be used to calibrate the parameters of the model. The calibration strategy consisted of fitting the calculated and experimental pore water and solid phase profiles values by tuning the values of the kinetic constants of the redox reactions (Figure 2). Once the fitting was optimized by trial and error, the mass fluxes of the elements between the different phases were computed. The mass fluxes in the aqueous phase through the Water-Sediment Interface (WSI) were calculated with the Fick's law. The fluxes involved in the reactions between the pore water and the solid phases were calculated from the time and depth integration over one year and 20 cm of sediment of the rates calculated for each reaction and discretization volume.

RESULTS

When present in the water reservoir, dissolved oxygen (DO) was consumed within the uppermost 0.5 cm of sediment. During the stratification season, however, no oxygen penetration was found (Figure 2). Pore water sulfate concentrations drastically decreased below the WSI, whereas H_2S , which was zero at the overlying water, peaked between 1 and 4 cm depth. The concentration of H_2S in pore water is mainly controlled by the sulfidization of the OM and, in less extent, by the precipitation of metal sulfides. Labile OM was consumed by O_2 , Mn-oxide, Fe-oxide and SO_4 at the first cm depth. As a result of Fe-Oxide and SO_4 reduction by OM, pH sharply increased below the SWI.

Pore water concentrations of Fe(II) and As were always higher than those in the overlying water, due to the reductive dissolution of the As-bearing Fe-oxide sedimented under oxic conditions. The pore water depth profile of Fe(II) and As was completely different when comparing oxic and anoxic conditions. Thus, a peak in the concentration of both elements is observed below the SWI under oxic conditions. Similar to Fe-oxides, Mn-oxides were also reduced in the uppermost cm of the sediment, Mn(II) was released to the pore water and precipitated as MnCO_3 . However, Mn concentrations are always one to two orders of magnitude lower than Fe. As a result of the drastic increase of pH, the Al concentration in pore water dropped below detection level just below the SWI. This is attributed to the precipitation of

amorphous $\text{Al}(\text{OH})_3$. Zinc, Cu, Co, and Ni, diffused from the overlying water and precipitated as metal sulfides in the shallowest cm of the sediment. Under anoxic conditions, trace metal sulfides reached the top of the sediments. However, when oxygen was present in the water reservoir metal sulfides concentration decreased close to the SWI, due to oxygen penetration. This means that the metal sulfides that were precipitated in the shallowest sediment during anoxic conditions were oxidized under oxic conditions releasing the metals to the pore water.

INTEGRATED ANNUAL FLUXES

The depth integrated annual fluxes of the elements between the different compartments are plotted in Figure 3. The results show that OM was mainly consumed by SO_4 and in minor proportion by Fe(III) and O_2 . The consumption of the OM by sulfate is overwhelming (82%), due to the absence of O_2 and Fe(III) fluxes through the upper boundary during most of the year. Dissolved O_2 was mainly consumed by the oxidation of OM and to a lesser extent by Fe(II). Under O_2 -oscillating concentration (holomictic), the oxidation of H_2S , FeS, FeS_2 and other metal sulfides during the oxic period represents the consumption of around 17% of total oxygen. Sulfides form up to the WSI in the anoxic period and are oxidized during the oxic period. Thus, 45% FeS and 30% trace metal sulfides precipitated under anoxic conditions were reoxidized under oxic conditions. The OM sulfidization (S-OM) represented the main sink for sulfide being the 60% under permanently oxic conditions and 79% under oxic conditions.

REFERENCES

- Torres, E. and Auleda, M. (2013): A sequential extraction procedure for sediments affected by acid mine drainage. *Journal of Geochemical Exploration* **128**, 35–41.
- & Ayora, C., Canovas, CR, Garcia-Robledo E., Galván L., Sarmiento A.M. (2013): Metal cycling during sediment early diagenesis in a water reservoir affected by acid mine drainage. *Science of the Total Environment*, **461-462**, 416–429.
- Van Cappellen P. and Wang, Y.F. (1996): Cycling of iron and manganese in surface sediments: a general theory for the coupled transport and reaction of carbon. *American Journal of Science*, **296**, 197–243.