



Metal cycling during sediment early diagenesis in a water reservoir affected by acid mine drainage



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HIGHLIGHTS

- This is the first complete diagenetic study of sediments affected by AMD and oscillating O₂ conditions.
- Unlike marine and lake systems, the low pH of the Sancho makes metals mobile.
- The Fe concentration in pore water is always higher than H₂S.
- The H₂S generated by sulfate-reduction is entirely precipitated as sulfides.
- Fast consumption of the O₂ due to OM and especially sulfide oxidation
- The sediment acts as sink for only less than 10% of metals dissolved in the reservoir.

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ABSTRACT

The discharge of acid mine drainage (AMD) into a reservoir may seriously affect the water quality. To investigate the metal transfer between the water and the sediment, three cores were collected from the Sancho Reservoir (Iberian Pyrite Belt, SW Spain) during different seasons: turnover event; oxic, stratified period; anoxic and under shallow perennially oxic conditions. The cores were sliced in an oxygen-free atmosphere, after which pore water was extracted by centrifugation and analyzed. A sequential extraction was then applied to the sediments to extract the water-soluble, monosulfide, low crystallinity Fe(III)-oxyhydroxide, crystalline Fe(III)-oxide, organic, pyrite and residual phases. The results showed that, despite the acidic chemistry of the water column (pH <4), the reservoir accumulated a high amount of autochthonous organic matter (up to 12 wt.%). Oxygen was consumed in 1 mm of sediment due to organic matter and sulfide oxidation. Below the oxic layer, Fe(III) and sulfate reduction peaks developed concomitantly and the resulting Fe(II) and S(II) were removed as sulfides and probably as S linked to organic matter. During the oxic season, schwertmannite precipitated in the water column and was redissolved in the organic-rich sediment, after which iron and arsenic diffused upwards again to the water column. The flux of precipitates was found to be two orders of magnitude higher than the aqueous one, and therefore the sediment acted as a sink for As and Fe. Trace metals (Cu, Zn, Cd, Pb, Ni, Co) and Al always diffused from the reservoir water and were incorporated into the sediments as sulfides and oxyhydroxides, respectively. In spite of the fact that the benthic fluxes estimated for trace metal and Al were much higher than those reported for lake and marine sediments, they only accounted for less than 10% of their total inventory dissolved in the column water.

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1. Introduction

Weathering of iron sulfides produces acid mine drainage (AMD) that contains high levels of sulfate, iron and other metals (Al, Cu, Cr,

Pb, Zn, Cd) and metalloids such as As, which constitute a major environmental concern (Nordstrom, 2011). The Tinto and Odiel Rivers have been heavily contaminated by decades of sulfide mining in the Iberian Pyrite Belt, SW Spain (Sanchez-España et al., 2005; Sarmiento et al., 2009a). The Odiel Basin is practically unregulated due to its AMD contamination. However, the Spanish National Hydrological Plan foresees the construction of two reservoirs, the Coronada (800 hm³) and Alcolea (363 hm³), for agricultural use. The Hydrological Plan is currently being drawn up in line with the Water Framework Directive (2000/60/EU),

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which aims to guarantee the quality of surface water. Within this framework, the cycling of toxic metals in reservoirs affected by AMD is a key issue. Thus, the effects of AMD discharges in lakes (Herlihy and Mills, 1985; Peine and Peiffer, 1996; Frommichen et al., 2004) and open-cut mine lakes (Ramstedt et al., 2003; Knoller et al., 2004; Denimal et al., 2005) have been documented. However, few studies of the impact of AMD on water reservoirs have been conducted (Nordstrom et al., 1999; Munk and Faure, 2004; Sarmiento et al., 2009b).

AMD can carry high loads of metals as dissolved species. Moreover, during floods, large quantities of Fe and Mn oxides are eroded from the source mining areas and transported as particulates in suspension (Cánovas et al., 2007); these can contain variable amounts of As, Pb, Cu and Cr as adsorbed and co-precipitated species (Alpers et al., 1994; Smith, 1999; Casiot et al., 2003). In water reservoirs, the particulate materials are incorporated into the sediment, where biogeochemical transformations might occur depending on the organic carbon supply and redox conditions.

Diagenetic processes have been extensively studied during the past few decades in both marine and lake sediments. The bacteria-mediated consumption of organic matter is coupled with the reduction of several oxidants in a well-known sequence (Raiswell and Canfield, 2012). The reduction of Fe(III)-hydroxides releases Fe and trace elements into the pore water, whereas the H₂S from sulfate reduction precipitates them as sulfides. The Fe(III) and sulfate reductions are both important processes in water reservoirs affected by AMD compared to marine and lacustrine sediments. Thus, although sulfur and iron distribution and diagenesis have been studied in sediments of lakes receiving AMD (Carignan and Tessier, 1988; Herlihy et al., 1988; Wicks et al., 1991), such studies have not focused on trace metal transformations. Conversely, trace metal cycling has been investigated in estuaries (Douglas and Adeney, 2000; Tang et al., 2002; Burton et al., 2005;), in lakes (Huerta-Diaz et al., 1998; Gallon et al., 2004; Couture et al., 2010) and in riverine sediments (Lesven et al., 2008, 2010). However, the pH and the low mobility of metals in such environments are very different from those of AMD.

Moreover, reservoirs may undergo water stratification and mixing (turnover) periods during the course of a year, leading to a periodic oscillation of oxygen concentration in the bottom water from completely anoxic during the stratified period to oxic during the turnover. The redox conditions strongly affect the iron and sulfur cycles and, therefore, the bioavailability of associated trace elements (Berner, 1984; Audry et al., 2006).

The present study was conducted to develop new insights into the biogeochemical behavior of trace metals in the bottom water and sediment from an AMD-affected water reservoir. Understanding metal cycling under fluctuating oxygen conditions is especially important to the calculation of net metal fluxes at the water–sediment interface. This boundary condition is required for accurate predictive modeling of water quality in planned reservoirs, especially those affected by AMD. To accomplish this, an AMD-affected water reservoir (Sancho) in southwestern Spain was studied. Since the Sancho Reservoir is holomictic (one turnover per year), core samples were collected during different seasons to investigate metal cycling under fluctuating oxygen conditions. Major and trace element concentrations were measured in both the pore water and solid phases.

2. Methods

2.1. Study site

The Sancho Reservoir (58 hm³) is located on the Odiel Basin in SW Spain (Fig. 1). The reservoir has a surface area of 427 ha and a maximum depth of 40 m. The River Meca, the main tributary of the Sancho Reservoir, is heavily contaminated by AMD with high concentrations of trace metals, iron and sulfate, and a mean pH of 2.6 (Galván et al., 2009, 2012). The average stream flow is 61 hm³/year, most of which occurs during a few winter floods. The reservoir was built in 1962 to

supply water for a paper mill refrigeration system. The water was initially neutral, but became acidic with time after the Tharsis mine closed in 1999 and water treatment ceased. The Sancho Reservoir has now a pH of around 3.5. There is little agricultural and industrial activity in the Odiel Basin, resulting in a low input of nutrients; however, until recently, sewage from a nearby village of about 1000 habitants was discharged into the reservoir. Despite the acidity of the water, biological activity seems to be present in the reservoir as significant total organic carbon (TOC) content has been found in the sediments. The reservoir fluctuates seasonally from mesotrophic to slightly eutrophic (OECD, 1982), and is holomictic, with two marked seasons. During the winter months, the entire water column is mixed (turnover), and dissolved oxygen reaches the sediment. During the rest of the year, the water column is stratified, and anoxic conditions develop deeper than 15 m due to oxidation of the dissolved organic matter.

2.2. Sample collection and onsite measurements

This study was based on three sediment samples collected in the central and deepest part of the reservoir (A_{ox} and B_{anox}) and close to the river entrance (C_{p_ox}). The location and main description are given in Table 1. During sampling, point A_{ox} was under oxidizing conditions (turnover) and point B_{anox} was under hypoxic conditions (stratified period). Point C_{p_ox} was always under oxidizing conditions. Points A_{ox} and B_{anox} are affected by oxygen fluctuations in the hypolimnion due to formation of the thermocline–oxycline (Fig. 1). For each sediment sampling point, samples of the column water were collected at depths of 2, 17 and 30 m (epilimnion, thermocline and hypolimnion, respectively). Point C_{p_ox} is shallower than the thermocline and only one water sample was collected from a depth of 2 m.

Sediment traps were installed to characterize the phase minerals and estimate the accumulation rates. The traps consisted of vertical tubes (6 cm diameter × 50 cm) that were installed during one hydrological year (September 2009–2010) at two sites of the reservoir (two in the center—points A and B—at depths of 30 and 33 m, and two close to the river entrance—point C—at 5 and 7 m depths). The traps were always installed more than 3 m from the bottom to prevent the recollection of re-suspended material.

Sediments were sampled using a parallel gravity corer (UWITEC, Austria) and plexiglass tubes of 60 cm long. The resulting cores comprised about 30 cm of sediment and 30 cm of the overlying water, which was analyzed as bottom water. The cores were protected from light to prevent photo-oxidation, and stored on ice at around 4 °C until returned to the laboratory the same day. For points B_{anox} and C_{p_ox}, dissolved oxygen (DO) and H₂S of the pore water were analyzed in the first 5 cm of sediment using microelectrodes. The cores were maintained under a N₂ flux to prevent oxidation of the reduced species. Microelectrodes were connected to a Multimeter (Unisense©) and mounted in a motorized micromanipulator (MC-232, Unisense©). Both Multimeter and micromanipulator were connected to a computer and controlled by the Sensor Trace PRO software (Unisense©). The H₂S microsensor was not sensitive to HS[−] and S^{2−}, but only to gaseous H₂S (Revsbech et al., 1983). The overlying water (bottom water) was then sampled and removed, and the cores were cut into diametral sections 1 to 2 cm thick in a N₂-purged glove box isolator and transferred into 50 mL centrifuge vials. Pore water was subsequently separated by centrifugation (3000 rpm, 15 min), after which physicochemical parameters (Eh, pH, T) were measured in a N₂ atmosphere inside the glove box. The pH and Eh were measured using a PH25 meter (Crison®) calibrated using 2 points (240–470 mV) and 3 points (pH 4.01–7.00–9.21), respectively. Redox potential measurements were corrected to the Standard Hydrogen Electrode. The sediment was then freeze-dried and stored in the centrifuge tubes in a dry atmosphere until sediment analysis.

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