

Geochemical Controls of Two Water Reservoirs that Receive Acid mine Drainage in the Odiel Basin

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INTRODUCTION.

Oxidation on the surface of sulphides produces an extremely acidic mine drainage (AMD) that contains high levels of sulphate, iron and other metals and metalloids (Al, Cu, Pb, Zn, As, Cd, etc.), and constitute a major environmental issue (Nordstrom and Alpers, 1999). The Tinto and Odiel Rivers drain materials from the Iberian Pyrite Belt, which has important massive sulfide deposits, with original reserves of 1700 million tons. As a result, the basin is highly contaminated by AMD (Cánovas et al., 2007; Sarmiento et al., 2009). Although mining activity is nowadays very scarce, the rivers still release to the ocean a significant percentage of the global flux of metals from the continents (Nieto et al., 2007).

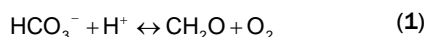
The Odiel basin is practically unregulated due to its extreme contamination. However, the Spanish Hydrological Plans foresee the construction of two new reservoirs for agricultural uses: the Coronada (800 hm³) and Alcolea (363 hm³) reservoirs. The initial estimates on the Alcolea reservoir are that, untreated, the water from this reservoir will be acid with high levels of aluminium and other toxic elements, rendering it unusable for irrigation. However, detailed modeling predictions on the amount and quality of the water expected in the reservoirs are needed.

For this purpose, the hydrogeochemical behaviour of two existing reservoirs is investigated. Olivargas and Sancho reservoirs, with capacities of 29 and 58 hm³, respectively, are located in the upper and middle part of the Odiel basin, where the main sources of mine contamination are located. Both receive acid mine effluents and despite this fact, the water in the Olivargas reservoir has neutral pH, whereas in the Sancho

reservoir the water has pH values close to 4 and decreasing with the years (Sarmiento et al., 2009).

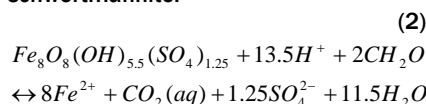
RESULTS AND DISCUSION.

In the Olivargas reservoir the oxycline is deeper than the thermocline, especially in summer season, indicating that the oxygen balance is partially controlled by the biological activity. The maximum production is in the metalimnion where the oxygen and light relation is the optimum for the biological activity (Wetzel, 2001). In this layer dissolved oxygen concentration increases from 7 to 15 mg O₂/L (Fig. 1) due to the photosynthesis:



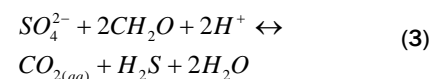
This is consistent with the fact that the pH values increase and electrical conductivity decreases. Anoxic conditions prevailed in the hypolimnion most of year. Under this reducing conditions pH values and EC increase while the Eh decreases. This behaviour will be discussed later in the metals and organic matter cycles.

In the Sancho reservoir the oxycline and thermocline are almost the same, which means that the oxygen concentration is independent of the weak biological and is controlled by the turbulent wind-mediated mixing. In the metalimnion all the oxygen is consumed during profile stratification. Due to this reducing conditions, Eh values decrease drastically and pH values increase significantly in the hypolimnion. These changes could be explained by the reduction of the dissolved and particulated Fe (III), such as schwertmannite:



This reaction is consistent with the pH increase observed in the hypolimnion (Fig. 1).

Close to the sediments, bacterial sulphate reduction could take place in addition to the iron hydroxides reduction:



This reaction is again consistent with the pH increase. As CO₂ (aq) is the major species at this pH (below 6) the increase of the electrical conductivity was not observed.

	Depth (m)	As (ppb)	Cd (ppb)	Pb (ppb)	Fe (ppm)	Mn (ppm)	Al (ppm)	Cu (ppm)
ene-09	2	<1	<1	2	0.1	0.39	0.0	0.01
	15	<1	<1	<1	0.0	0.41	0.0	0.01
	31	<1	1	<1	0.0	0.47	0.0	0.02
Olivargas	2	1	<1	<1	0.0	0.06	0.0	0.00
	8	1	<1	<1	0.0	0.06	0.0	0.00
	29	<1	<1	<1	0.0	0.76	0.0	0.01
bottom	5	<1	4	2.5	8.26	0.0	0.01	
ene-09	2	1	4	3	0.2	2.79	3.6	0.47
	12	1	4	3	0.2	2.77	3.6	0.46
	25	<1	4	3	0.2	2.75	3.6	0.46
Sancho	2	<1	5	6	0.2	3.18	5.2	0.64
	16	<1	5	5	0.2	2.89	5.3	0.57
	29	<1	<1	<1	4.2	2.99	5.4	0.01
	bottom	2	1	1	6.8	3.19	4.3	0.30

Table 1. Concentration of some parameters along the profiles in both reservoirs (<dl indicates below detection limit)

Al concentration remains constant with depth, and only a small decrease is observed near the bottom as pH reaches 5.5. As Fe-hydroxysulfates are reduced and re-dissolved, adsorbed As is mobilized. The behaviour of the rest of metals is opposite. Dissolved Cu, Cd, Pb and Zn concentrations decrease in the hypolimnion (Table 1). The reason for that is not clear, and could it be due to the enhancement of adsorption onto clay, organic matter and even Al-hydroxide particles as pH increases.

The Olivargas reservoir shows a different behavior for Fe. Due to the near neutral pH, Fe is absent into the water column. However, Fe and Mn concentration

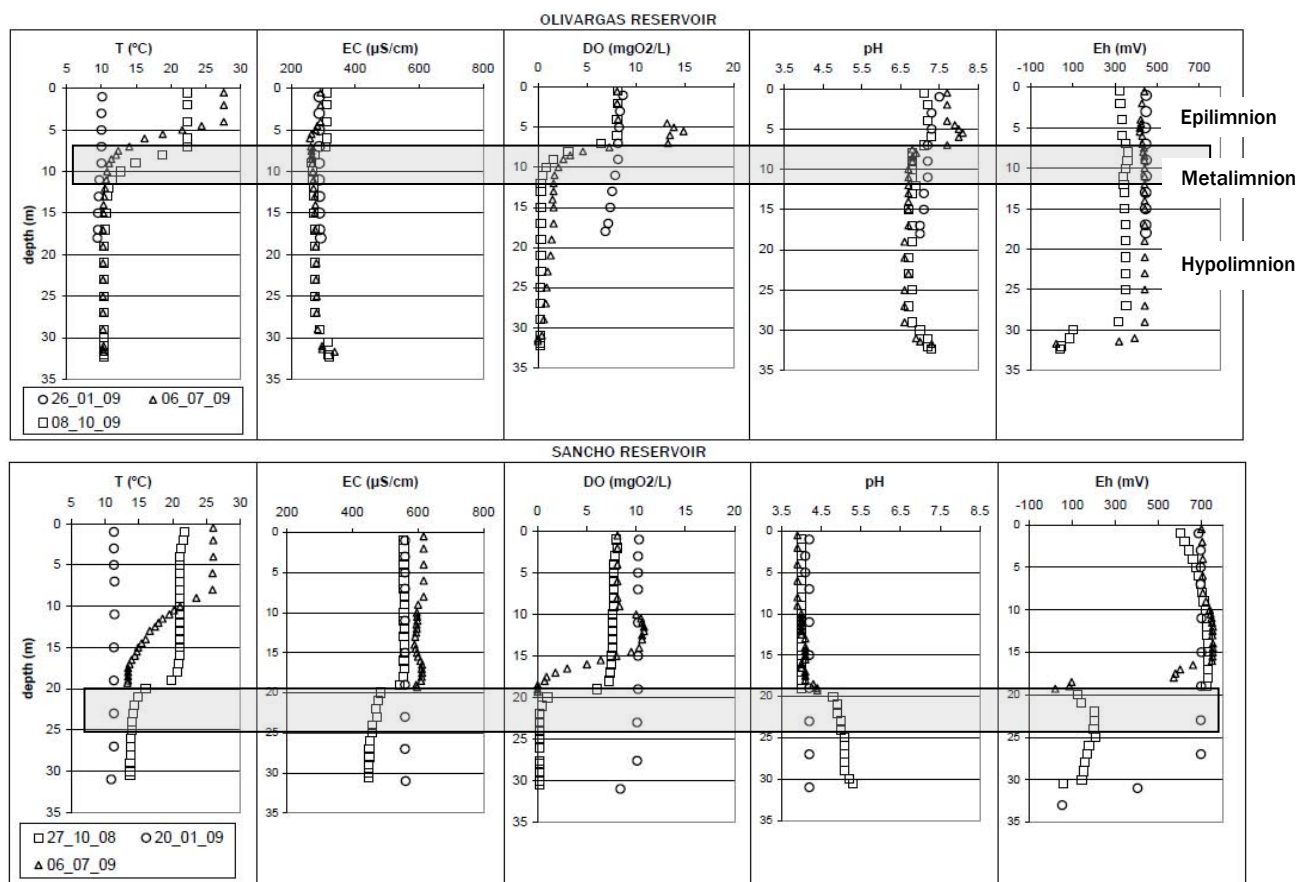
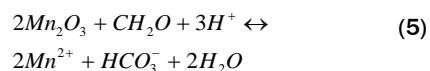
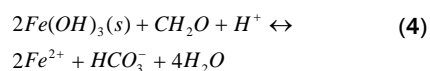


Fig 1. Distribution of Temperature, EC, DO, pH and Eh values versus depth.

increases significantly near the bottom due to the reduction and re-dissolution of the Fe and Mn hydroxides carried by periodical floods:



These two reactions are also consistent with the pH and EC evolution in the water column (Fig. 1).

CONCLUSIONS.

The Olivargas and Sancho reservoirs behave as holomictic lakes showing thermal stratification during most of the year and homogenization during January. Sancho reservoir is less stable than Olivargas and its thermocline is deeper. In Olivargas reservoir oxycline is deeper than thermocline due to its meso-eutrophic conditions and to the higher photosynthetically productivity, specially during summer.

In the Sancho reservoir, the high acidity input and the poor biological activity

result in an acidic pH. Under pH 4, Al is found in significant concentrations in solution. Estratification causes an oxic epilimnion and an anoxic hypolimnion, with high impact in the metal cycling. Fe (III) shows low mobility in the epilimnion, whereas Fe (III) minerals and adsorbed As (V) are remobilized under the anoxic conditions of the hypolimnion, whereas Cu, Cd, Pb and Zn show opposite behaviour.

In the Olivargas reservoir, the lower acidity input, and the higher biological productivity maintains the pH neutral. Al and metals are not mobile. However, the anoxic conditions of the hypolimnion cause the Fe and Mn hydroxides to re-dissolve, and As and Pb to desorb.

ACKNOWLEDGMENTS.

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REFERENCES.

- Cánovas, C.R., Olías, M., Nieto, J.M., Sarmiento, A.M., Cerón, J.C. (2007): Hydrogeochemical characteristics of the Tinto and Odiel rivers (SWSpain). Factor controlling metal contents. *Sci Total Environ* **373**, 363–82.
- Nieto, J.M., Sarmiento, A.M., Olías, M., Cánovas, C.R., Ayora, C. (2007): Acid mine drainage pollution in the Tinto and Odiel rivers, SW Spain. 12th Symposium on Water-Rock Interaction (Kunming, China). *Abs.* **2**, 1251-1254
- Nordstrom, D.K., Alpers, C.N., Coston, J.A., Taylor, H.E., McCleskey, R.B., Ball, J.W., Ogle, S., Cotsifas, J.S., Davis, J.A. (1999): Geochemistry, toxicity, and sorption properties of contaminated sediments and pore waters from two reservoirs receiving acid mine drainage. *U.S.G.S Water Resources Investigations Report*, 289-296.
- Sarmiento, A.M., Olías, M., Nieto, J.M., Cánovas, C. R., Delgado, J. (2009): Natural attenuation processes in two water reservoirs receiving acid mine drainage. *Science of the Total Environment*, **407**, 2051-2062.
- Wetzel, R.G. (2001): *Limnology. Lake and river ecosystem*. 3rd ed. San Diego. Academic Press. xvi, 1006 pp.