

# Bacterial Sulphide Precipitation in the Water Column of an Acidic Pit Lake

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## INTRODUCTION

A 10 m-thick turbidity layer has been detected in the acidic pit lake of Cueva de la Mora, Iberian Pyrite Belt (SW Spain) (Sánchez-España et al., 2010). This turbidity layer appears immediately below the redoxcline, and shows an intense turbidity maximum at ~10 m, and decreases again to near-zero values at ~20 m depth.

This turbidity layer is closely related to the activity of sulphate-reducing bacteria (SRB), (Wendt-Potthoff et al., 2011). Vertical profiles of bacterially-induced H<sub>2</sub>S (g) have been measured in different seasons. This H<sub>2</sub>S reacts with the dissolved metals which, in turn, lead to the formation of different sulphides. The H<sub>2</sub>S profiles show a similar shape to the turbidity profile, thus suggesting that the turbidity of this lake mostly results from the presence of biogenic sulphide precipitates.



fig 1. Field view of Cueva de la Mora pit lake (Huelva).

## STUDY SITE

The acidic pit lake of Cueva de la Mora (Fig. 1) was formed after the abandonment of its mining activity in 1971.

In spite of its small size (38 m max. depth, 0.28 Hm<sup>3</sup> volume, 1.76 m<sup>2</sup> surface area), this lake represents a hydrologically and biogeochemically

complex system. Apart from its acidic pH (2.2-4.5) and its high metal and sulphate content typical of the pit lakes of this area (Sánchez-España et al. 2009), Cueva de la Mora shows a high nutrient content which favours an intense microbial activity in the sediment as well as in the water column (Wendt-Potthoff et al., 2011).

## METHODS

A study of this turbidity layer has been undertaken, including:

- recording of vertical profiles of turbidity, temperature, conductivity, Eh, pH, chlorophyll-a and photosynthetically active radiation (PAR) and dissolved oxygen (DO) in different periods with multiparametric probes (DS5 and MS5 from Hydrolab);
- detailed sampling and chemical analysis of specific sections of the water column;
- mineralogical and chemical analyses of suspended particulate matter (SPM) by XRD, XRF, SEM-EDS and acid-digestion followed by chemical analysis by ICP-AES. These analyses included particles retained in the filters during filtration, as well as chemical precipitates found in sediment traps and mineral traps placed at depths of 11 and 19 m (Yusta et al. 2011).

## RESULTS AND DISCUSSION

### Seasonal Variation of Turbidity

The turbidity layer appears at 10 m depth, just when the Eh value drops below 400 mV (Fig. 2) and all dissolved iron is present as ferrous iron (Fe<sup>2+</sup>). This finding may be biogeochemically relevant as it may imply either inhibition by ferric iron and/or competition by iron-reducing bacteria (FeRB) for organic carbon (Wendt-Potthoff et al., 2011).

Below that depth, H<sub>2</sub>S (g) is formed (Fig. 3a) as a product of the sulphate-reducing bacteria (SRB) metabolism represented by equation 1 (where organic matter is simplified as CH<sub>2</sub>O).

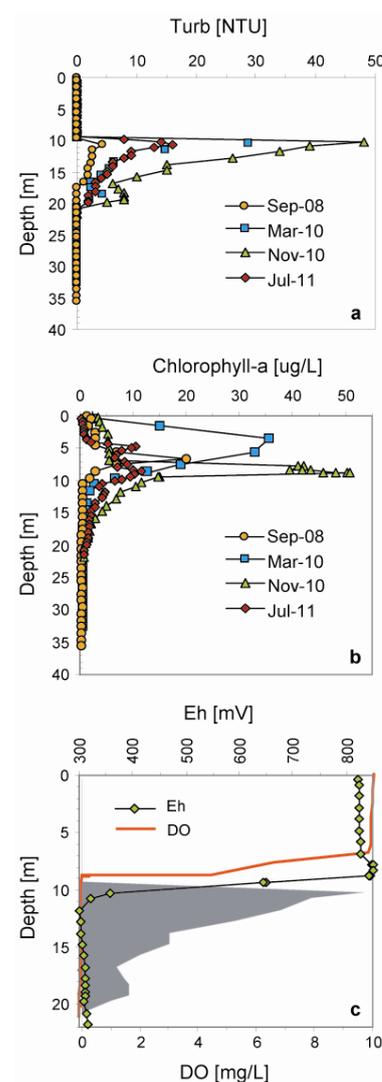
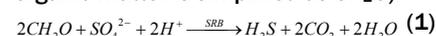


fig 2. Vertical profile of turbidity (a) and chlorophyll-a (b) in different seasons; profiles in (c) show the relation between Eh, DO and the occurrence of the turbidity layer (shaded area) in November 2010.

**palabras clave:** Lago ácido de Mina, Turbidez, Sulfato-Reducción, Sulfuros.

**key words:** Acidic pit lake, Turbidity, Sulphate Reduction, Sulphides.

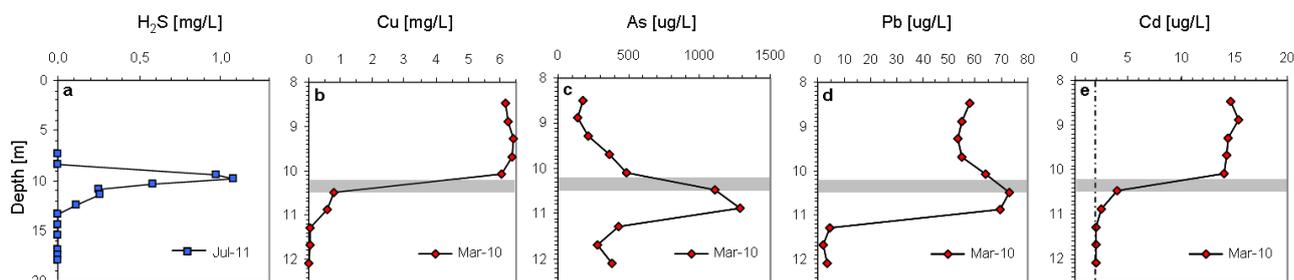


fig 3. Vertical profiles of concentration of H<sub>2</sub>S (a), Cu (b), As (c), Pb (d) and Cd (e). The gray area represents the location of the turbidity maximum.

A close positive correlation has been found between the intensity of the turbidity peak and the phytoplanktonic biomass, as deduced from the profiles of turbidity and chlorophyll-a (Fig. 2a-b).

This finding highlights the role of phytoplanktonic communities as primary producers of carbon sustaining the planktonic and benthic microbial activity of the lake.

**Turbidity Composition**

The most relevant consequence of the bacterial H<sub>2</sub>S generation is the Cu precipitation as a Cu-sulphide, which results in the total removal of this metal from the water column (initially present at a concentration of 6 mg/L) (Fig. 3b). This fact is confirmed by the chemical analysis of the SPM that cause the turbidity (Fig. 4), by the identification of amorphous CuS in the sediment traps (Fig. 5), as well as by the synthesis of crystalline CuS by addition of Cu<sup>2+</sup> to a sample from the SRB-active layer initially without any Cu content (Fig. 6)

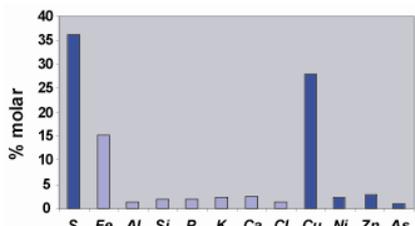


fig 4 XRF semiquantitative chemical analyses of suspended particulate matter at the maximum turbidity depth.

The SRB activity also provokes the precipitation of many other metals present in the water. The solubility constants for metal sulphides approximately follow the sequence: Cu << Cd < Pb < Zn << Fe < Ni (Hao et 1996). The precipitation of these other sulphides provokes the removal of other trace metals like Pb and Cd (Fig. 3d-e), although this fact is not reflected in the chemical composition of SPM due its very low content. The opposite case applies for Zn and Ni, which contributed

with 2-3% to the molar percentage of the SPM (Fig 4) but show virtually no decrease in their respective concentration.

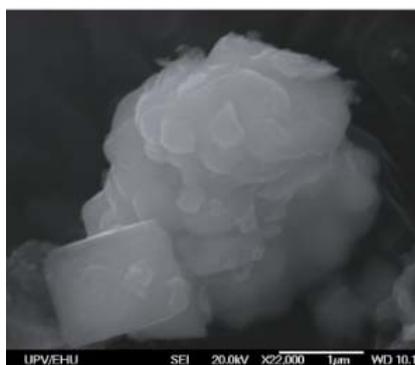


fig 5. SEM image of CuS retained in the sediment trap located at 19 m depth.

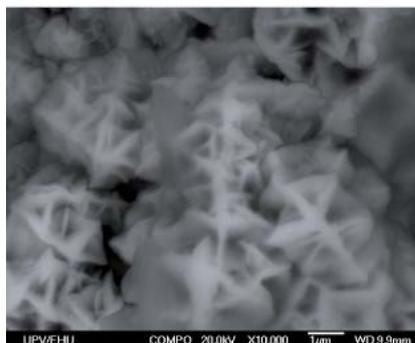


fig 6. SEM image of CuS obtained by adding Cu<sup>2+</sup> to a water sample from 12 m depth.



fig 7. SEM image of arsenic sulphide retained in the sediment trap located at 19 m depth.

Although the behaviour of As is commonly reported to be associated to

the absorption into schwertmannite (Regenspurg and Peiffer, 2005), we have also found clear evidence of As sulphide formation in the sediment traps (Fig. 7). This As-sulphide precipitation also results in a sharp decrease in its concentration in this layer (Fig. 3c).

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**REFERENCES**

Hao, O.J., Chem, J.M., Huang, L., Burglass, R.L. (1996): Sulfate-reducing bacteria. *Crit Rev Environ Sci Technol* **26**, 155-187.  
 Regenspurg, S., Peiffer, S. (2005): Arsenate and chromate incorporation in schwertmannite. *Applied Geochemistry* **20**, 1226-1239.  
 Sánchez-España, J., López-Pamo, E., Díez-Ercilla, M., Santofimia, E. (2009): Physico-chemical gradients and meromitic stratification in Cueva de la Mora and other acidic pit lakes of the Iberian Pyrite Belt. *Mine Water Environ*, **28**, 15-29.  
 Sánchez-España, J., Yusta, I., Díez Ercilla, M. (2010): SEM-EDS Study of a mine pit lake turbidity layer: Biogeochemical and environmental aspects. *Macla* **13**, 193-194.  
 Wendt-Potthoff, K., Koschorreck, M., Díez Ercilla M., Sánchez-España J. (2011): Microbial activity and biogeochemical cycling in a nutrient-rich meromitic acid pit lake. *Limnológica*, in press, <http://dx.doi.org/10.1016/j.limno.2011.10.004>  
 Yusta, I., Sánchez-España, J., Díez-Ercilla, M., Falágan, C. (2011): Sampling devices for monitoring dissolution and precipitation reaction in acidic mine lakes: sediment traps vs. precipitation traps. *Macla* **15**, 201-202.