Monimolimnetic gradients in meromictic pit lakes of the Iberian Pyrite Belt (SW Spain): physico-chemical description

Javier Sánchez España, Enrique López Pamo, Marta Diez, Esther Santofimia

Instituto Geológico y Minero de España (IGME), Rios Rosas, 23, 28003, Madrid, Spain,
e-mail: j.sanchez@igme.es

Abstract
A marked vertical trend of increasing temperature and dissolved metals is observed in the monimolimnion of some meromictic pit lakes of the Iberian Pyrite Belt. Such a gradient suggests the existence of a reactive bottom in which several chemical reactions (e.g., pyrite oxidation by Fe^{3+}, redissolution of Fe^{3+} mineral particles) and/or microbial processes (e.g., bacterial reduction of Fe^{3+} and SO_4^{2-} coupled with fermentation of dissolved organic matter), could be taking place. A more complex model involving density currents along the pit lake contours, or inflow of denser and hotter metal-sulphate-laden groundwater from former galleries and ramps should not be entirely discarded.

Key words: Stratification, meromixis, mine pit lakes, bacterial reduction, chemical gradients

Introduction
The majority of the mine pits developed during the 20th century in the Province of Huelva were abandoned and progressively flooded by the entrance of groundwater and mine drainage from galleries and waste piles. At present, 22 pit lakes with highly acidic water containing high metal and sulphate concentrations have been recognized in the Iberian pyrite belt (IPB) (Sánchez-España et al., 2008). As a whole, these pit lakes contain around 25 Hm^3 of acid mine drainage (AMD), which probably represents one of Europe's largest accumulations of AMD. In addition, some of the pits are still flooding and will continue to grow (e.g., Corta Atalaya, Cerro Colorado, Aznalcollar), so the total amount of metal-polluted water in these pit lakes will significantly increase in the future.
Detailed limnological research is being conducted in selected pit lakes of the area. The principal aim of these studies is to compare the water chemistry and the stratification patterns among different pit lakes with distinct size, age, geometry, and depth, as well as the physical, geochemical, and microbial controls on the pit lake water composition and their temporal evolution. These data could serve in the future to aid the competent authorities and regulation agencies in the design of remediation/restoration alternatives for the recovery of such a strongly impacted mining area.

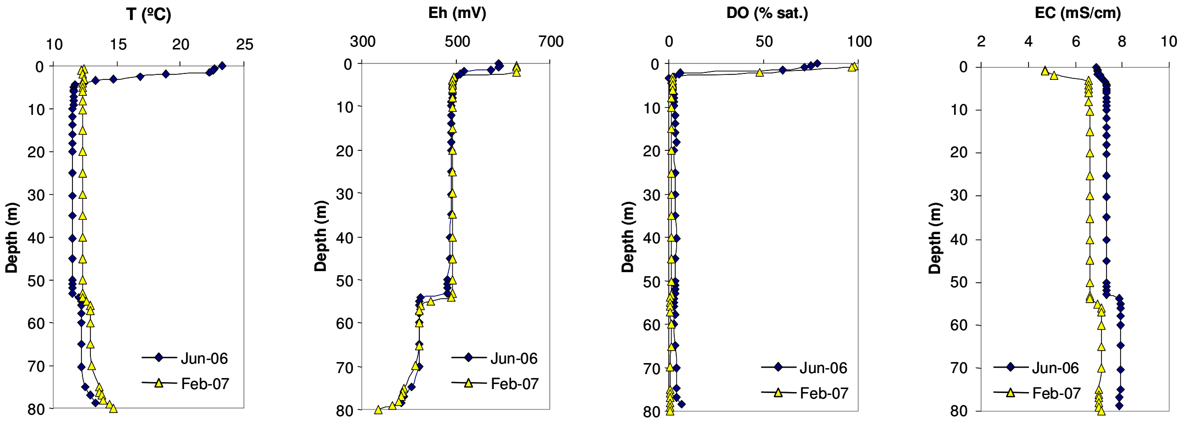
Results and Discussion
The pit lakes of the IPB are very diverse in size, depth, age, and water composition, but share a common geological framework and a chiefly meromictic model of lake stratification. The great majority of the studied pit lakes are meromictic and consistently stratified. They all have a well-defined chemocline, which separates an upper, oxygenated and lower density mixolimnion from a lower, anoxic and higher density monimolimnion, which is perennially isolated from the rest of the water column. The mixolimnion is seasonally stratified from early spring to late autumn, when a warmer and lighter epilimnion develops in the upper meters of the water column, overlying an intermediate metalimnion, and a lower and cooler hypolimnion. As regards to the monimolimnia, on-going research has revealed the existence of two distinct stratification patterns that seem to have no apparent relation with factors like size, depth, age, or local geology, but could be related to other parameters, such as pit geometry, groundwater flow, or mineralogy of the pit bottoms. In the simplest model, represented by pit lakes like San Telmo or Nª Sª del Carmen, the monimolimnion is chemically uniform and no vertical trend is recognized. In the more complex model, exemplified by Cueva de la Mora or Filón Centro (Tharsis), the monimolimnion shows a marked physico-chemical trend of increasing temperature and dissolved solids content. In a previous paper (Sánchez-España et al., 2007), we presented a hydrogeochemical and microbiological description of the first type of pit lakes with a study conducted in San Telmo. This paper reports some general characteristics of the stratified monimolimnia in the second type of pit lakes.

Physico-chemical stratification of the Confesionarios pit lake

The Confesionarios pit lake has a surface area of 24,800 m^2 and a maximum depth of 80 m. This lake contains around 1 Hm^3 of acidic water with a pH of 2.5-3.5 and high metal and sulphate concentrations (Sánchez-España et al., 2008). At an estimated age of about 120 years, it is considered the oldest pit lake in the IPB and therefore represents a mature stage within the IPB's spectrum.

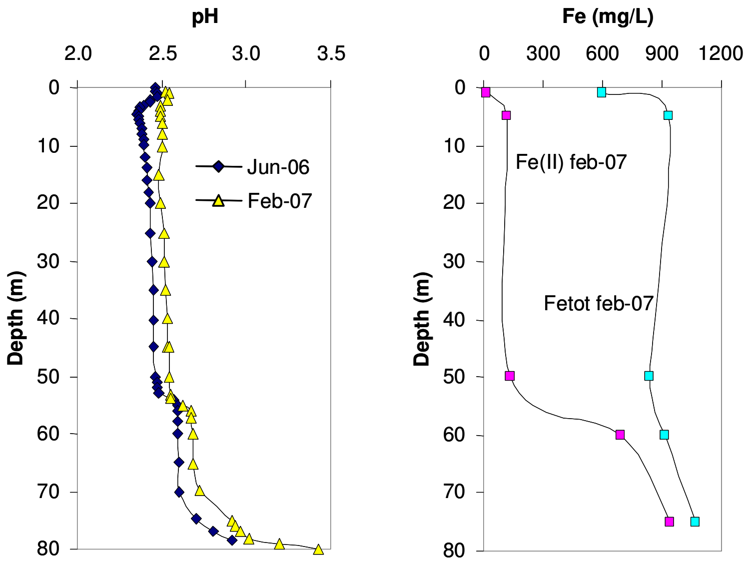
The Confesionarios pit lake has a thin mixolimnion around 4-5 m deep, and a monimolimnion with two different layers, an upper monimolimnion (from 5 to about 53 m in depth), which is chemically homogeneous, and a lower monimolimnion (from 53 to about 80 m in depth), which has a progressive gradient of temperature, Eh, pH, and Fe(II) concentration (Figure 1).

Figure 1 *Vertical profiles of temperature (T), Eh, dissolved oxygen (DO), and electrical conductivity (EC) in the Confesionarios pit lake.*



The lower monimolimnion is slightly warmer than the upper monimolimnion, but this stratification pattern is stable during the entire year. The upper monimolimnion is also thermally homogenized with the mixolimnion (Figure 1), but the density difference between both layers avoids a winter turnover and ensures a perennial chemical stratification. The geochemical difference observed between the monimolimnetic layers also affects the pH (2.5 in the upper monimolimnion and 2.7-3.4 in the lower monimolimnion) and the iron speciation and redox conditions (dissolved iron is predominantly ferric in the upper monimolimnion and chiefly ferrous in the lower monimolimnion; Figure 2). The chemical gradient towards the pit lake bottom may suggest some kind of upwards diffusion of dissolved constituents from a reactive sediment cover, although this is still to be checked.

Figure 2 *The pH and Fe(II)/Fe_{tot} profiles for the Confesionarios pit lake.*



Physico-chemical stratification of the Cueva de la Mora pit lake
Cueva de la Mora probably represents an outstanding example of chemical and density gradient within the monimolimnion. This pit lake has a surface area of 17,800 m^2 and a depth of 40 m. This mine was abandoned in the 1940's, so it also represents a mature stage of pit lake development with more than 60 years of hydrogeochemical evolution.
At present, the pit lake shows an upper mixolimnion of around 12 m in depth, and a lower sharply stratified monimolimnion of 30 m depth, which shows several sub-layers of increasing temperature, density, and metal-sulphate concentrations towards the lake bottom (Figures 3, 4, and 5).

***Figure 3** Temperature and pH profiles for the Cueva de la Mora pit lake in 2006 and 2007.*

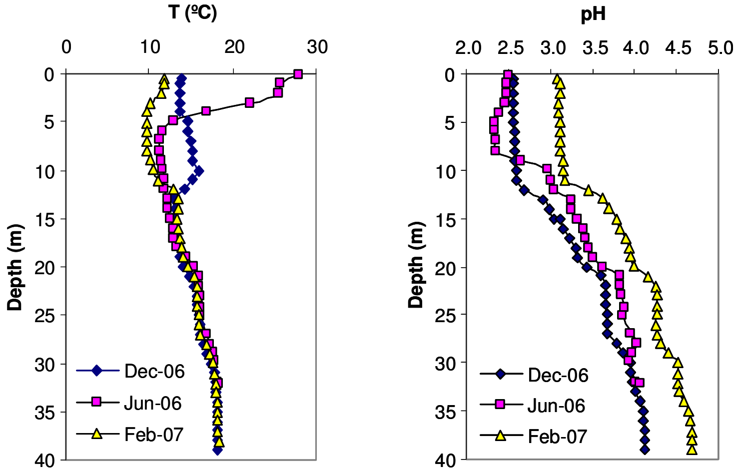
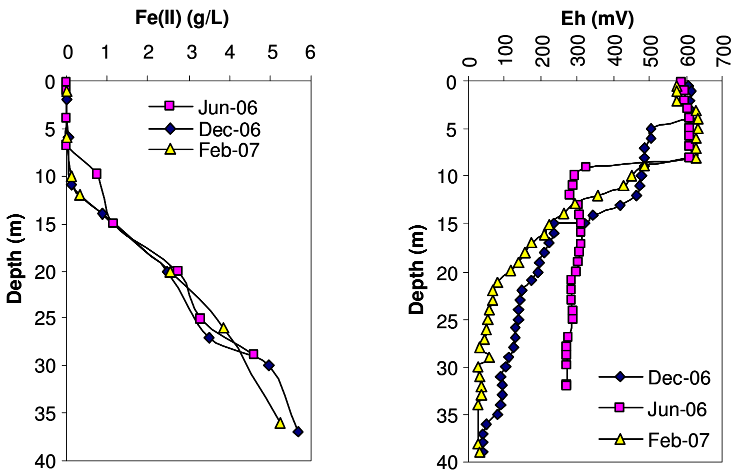
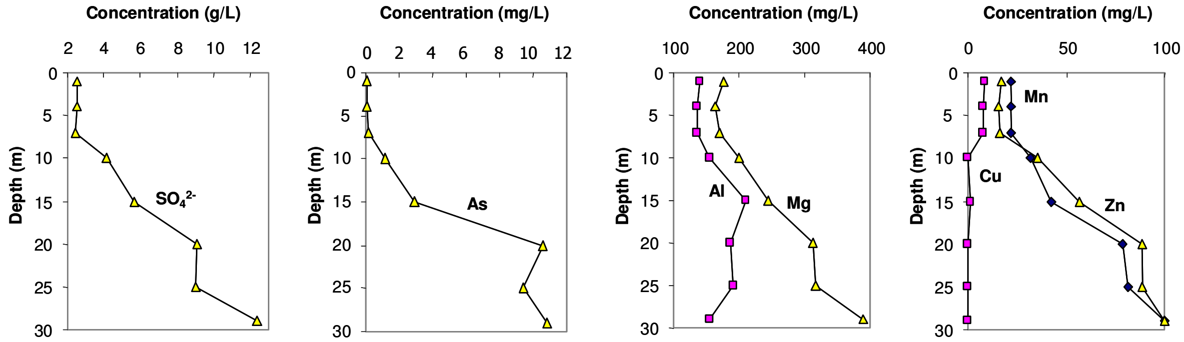


***Figure 4** Fe(II) and pH profiles for Cueva de la Mora pit lake in 2006 and 2007.*



The lake bottom is 4-6ºC warmer than the upper monimolimnion (18ºC and 12-14ºC, respectively), and is much less acidic (pH 4.1-4.7 *vs*. 2.7-3.1), and has much lower redox potential (-50 mV *vs*. 450 mV) and much higher ferrous iron concentrations (5.5 g/L *vs*. 1 g/L; Figures 3 and 4). The concentration of iron and other elements such as sulphate (12 g/L) and arsenic (around 10 mg/L) in the pit lake bottom are surprisingly high in comparison with the mixolimnetic water (2 g/L and <100 µg/L, respectively; Figure 5), and even to most AMD systems studied to date in the IPB (e.g., Sánchez-España et al., 2005). Mn and Zn concentrations also sharply increase with depth, and only Al and Cu show a reverse trend, which could be related to precipitation and sorption processes, respectively. This stratification pattern is very unusual among natural lakes (Wetzel, 2001) and even in similar environments such as the Berkeley pit lake (Gammons and Duaime, 2006).

Figure 5 *Vertical variation of the concentration of sulphate, arsenic, and selected metals (Al, Mg, Cu, Mn, Zn) in the Cueva de la Mora pit lake (Data from December 2005).*



The observed physico-chemical gradients resemble those observed in the Aznalcollar pit lake during the spill of 1.4 Hm^3 of pyrite wastes (Santofimia et al., 2006), which suggests the existence of a reactive pit lake bottom in which both abiotic and biotic reactions could be taking place. In fact, some presence of CO_2 and H_2S is expected (based on field evidence) in the monimolimnion, which points to the probable presence of sulphate-reducing bacteria which could be coupling this process with anaerobic oxidation of dissolved organic matter and with the reductive dissolution of ferric mineral particles (schwertmannite, jarosite) settled from the pit lake surface. Alternatively, this pattern of pit lake stratification could have been provoked by several factors like: (i) a singular geometry of the former pit contours, which could have favoured the existence of small euxinic basins isolated from local currents, (ii) the flushing of large amounts of soluble salts from the underground voids during the initial stages of lake formation, (iii) the presence of large amounts of pyrite outcropping in the pit bottom at the time of flooding, (iv) hydrogeological connection of the pit bottom with groundwater inflow from the mine shafts and galleries, or (v) a combination of all these factors.

Concluding remark

Given the independence of the factors that have contributed to this singular stratification pattern, it remains unclear why these pit lakes have developed such a physico-chemical gradient towards the pit lake bottom whereas others with similar age, size, depth, or geological framework have not. Further research is needed in order to resolve this question, which has an evident applied aspect. Future studies that will be conducted in the IPB pit lakes will include detailed chemical, mineralogical and microbiological investigations in the sediment-water interface, stable isotopic studies of waters and minerals, geochemical modeling, and laboratory and field experiments aimed at revealing geochemical and microbiological controls of the pit lake composition.

References

Gammons, C.H., Duaime, T.E. (2006). Long term changes in the limnology and geochemistry of the Berkeley pit lake, Butte, Montana. Mine Water and the Environment, 25, 76-85.

Sánchez-España, J., López-Pamo, E., Santofimia, E., Aduvire, 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. Applied Geochemistry, 20-7, 1320-1356.

Sánchez-España, J., López-Pamo, E., Santofimia, E., Diez, M. (2008). The acidic mine pit lakes of the Iberian Pyrite Belt: An approach to their physical limnology and hydrogeochemistry. Applied Geochemistry, DOI 10.1016/j.apgeochem.2007.12.036.

Sánchez-España, J., Santofimia, E., González-Toril, E., San Martín-Úriz, P., López-Pamo, E., Amils, R. (2007). Physicochemical and microbiological stratification of a meromictic mine pit lake (San Telmo, IPB). In R. Cidu and F. Frau (Eds.), Proceedings of the IMWA Symposium, 29-31 May 2007, Cagliari, Sardinia, Italy.

Santofimia, E., López-Pamo, E., Sánchez-España, J., Schultze, M., Friese, K.. (2007). Hydrogeochemical evolution of the Aznalcollar pit lake during the spill of a pyrite pile. In R. Cidu and F. Frau (Eds.), Proceedings of the IMWA Symposium, 29-31 May 2007, Cagliari, Sardinia, Italy.

Wetzel, D.B. (2001). Limnology. Lake and river ecosystems, 3rd Ed., *Academic Press*, San Diego, Calif., 1006 p.