Journal of Hydrology 511 (2014) 494–508

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Hydrological investigation of a multi-stratified pit lake using radioactive and stable isotopes combined with hydrometric monitoring

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ARTICLE INFO

Article history:
Received 22 March 2013
Received in revised form 17 October 2013
Accepted 1 February 2014
Available online 10 February 2014
This manuscript was handled by Laurent Charlet, Editor-in-Chief, with the assistance of Tamotsu Kozaki, Associate Editor

Keywords:
Pit lake
Acid mine water
Stratification
Groundwater dynamics
Flooding history
Stable isotopes

SUMMARY

The internal configuration and hydrological dynamics of meromictic pit lakes is often complex and needs to be studied by different tools including stable and radiogenic isotopes. This study combines a multi-isotopic approach (^3H_w, δ^2H_w, $\delta^{18}O_w$, $\delta^{34}S_{SO4}$) with meteorological, hydrological and hydrochemical monitoring to deduce the flooding history and hydrological dynamics of a meromictic and deeply stratified pit lake (Cueva de la Mora mine, SW Spain). The mine system is complex and includes horizontal galleries, shafts and large rooms physically connected to the mine pit. Specific conductance and temperature profiles obtained in the pit lake draw a physical structure with four monimolimnetic sub-layers of increasing density with depth. This characteristic stratification with m-scale layers separated by sharp transitional zones is rather unusual in other pit lakes and in most natural lakes. Tritium abundance in the different layers indicates that the deep lake water entered the pit basin between 1971 and 1972 which is coincident with the dates of mine closure. The oxygen and deuterium isotope composition of the different layers describes a marked and stable stratification, with an increasing evaporative influence towards the lake surface and a minimal influence of groundwater flow on the structure and composition of the monimolimnion. This study reveals that the initial stages of flooding (via influx of metal- and sulfate-loaded mine drainage from underlying galleries at different depths) may be essential to imprint a layered physical structure to pit lakes which would be very difficult to explain merely by physical processes. After reaching its present water level and morphology, the monimolimnion of this pit lake seems to have remained essentially isolated and chemically unmodified during decades.

1. Introduction

Pit lakes are a very special case of artificial lake formed after the abandonment and later flooding of open-pit mines by the influx of different waters (e.g., groundwater, precipitation, surface runoff, river water, acid mine drainage from adjacent mine galleries; Geller et al., 1998). Due to strong density gradients provoked by the elevated sulfate and metal contents of mine water input at depth, and also to their high depth to surface ratio (which normally exceeds those found in natural lakes) circulation currents cannot reach the bottom and these lakes may become *meromictic* (Anderson et al., 1985; Doyle and Runnells, 1997; Boehrer and Schultze, 2008). The form of the lake basin is not the only prerequisite for meromixis and the presence and influx of waters of different chemistry and density appears to be essential to form and sustain meromixis (Schultze and Boehrer, 2009). In meromictic lakes, the bottom-most part of the water mass (so-called *monimolimnion*), does not mix with the upper, seasonally-mixed layer (known as *mixolimnion*) for at least one hydrological year (Walker and Likens, 1975; Wetzel, 2001; Boehrer and Schultze, 2008). Because of its isolation from the atmosphere, elevated concentrations of reduced species (NH_4^+, Fe^{2+}) and gases (H_2S, CH_4, CO_2, N_2, H_2) may accumulate in the monimolimnion as a result of diverse biogeochemical processes. This type of lake offers a good opportunity to study the biogeochemical cycling of nutrients and metals across the redoxcline (e.g., Boehrer and Schultze, 2008; Wendt-Potthoff et al., 2012), often within a precisely defined timescale.

One of the highest concentrations of acidic pit lakes resulting from surface metal mining in Europe is presently observed in the *Iberian Pyrite Belt* (IPB), SW Spain, where more than 80 different mines have been exploited since Pre-Roman times until present-day

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http://dx.doi.org/10.1016/j.jhydrol.2014.02.003
0022-1694/

for S, Cu, Zn, Pb, Ag and Au (Pinedo Vara, 1963; Marcoux and Leistel, 1998). These deposits were mostly mined by underground works in ancient times, but the extensive mining carried out during the 19th and 20th centuries included the development of many open-pits. Therefore, the mine design usually includes a dense network of galleries and shafts connecting with an open pit at different levels (Pinedo Vara, 1963). Most of these mines were abandoned in the 1980s–90s. After mine closure and the subsequent cessation of pumping operations, most pits were progressively filled with the input of (i) acid mine drainage (AMD) entering the pit from adjacent underground mine workings, (ii) groundwater, (iii) surface runoff, and (iv) precipitation. As a result, more than 20 pit lakes of variable size have been formed in the IPB during recent times (Sánchez-España et al., 2008, 2009, 2013). These pit lakes are variable in age, depth, geometry, water chemistry, trophic state, and stratification style. Most lakes are very acidic (mostly, pH = 2.0–3.5) and contain elevated concentrations of metals (Fe, Al, Cu, Zn, As, Cr, Pb, Co, Ni, Cd), as well as high concentrations of microbially-related gases of potential environmental risk (commonly CO_2, but also lesser amounts of H_2S and CH_4) (Sánchez-España et al., 2008, 2009). Their often unique hydrological and biogeochemical features make these lakes large-scale laboratories for the study of different limnological and ecological aspects relevant to environmental science.

To date, the hydrological connection of the IPB acidic pit lakes with the surrounding mines and aquifers is not well understood, and therefore their impact on the water quality of local groundwater and creeks has not been adequately evaluated. A significant difficulty for the hydrological investigation of old pit lakes usually arises from the lack of information from the former mine companies. Detailed studies of pit lakes can be therefore very helpful to quantify the factors controlling their water chemistry, lake productivity, and stratification pattern, and may allow to build models for water quality evolution in future and presently-forming pit lakes.

Tritium (^3H) isotopes have been successfully applied in many hydrological studies to date modern (>1950s) meteoric waters and to calculate transit times in stream waters, aquifers and lakes (e.g., Clark and Fritz, 1997; Blum and Erel, 2005; Cook et al., 2005; Morgenstern et al., 2010). Tritium measurements have also been recently used in combination with SF_6 tracing to deduce lake water and groundwater ages in German pit lakes (Seebach et al., 2010). The stable isotopes of oxygen and hydrogen in water ($\delta^{18}O_W$, δ^2H_W) have been extensively used in hydrological studies of lakes (e.g., Zimermann, 1979; Gat, 1980, 1996; Walker and Krabbenhoft, 1998; Gibson et al., 2005; Henderson and Shuman, 2011), and have been applied in hydrological research of pit lakes to deduce lake water budgets, groundwater recharge, groundwater-surface water interactions and evaporation rates (e.g., Pellicori et al., 2005; Gammons et al., 2006, 2009; Hofmann et al., 2008; Seebach et al., 2008, 2010; Dietz et al., 2008). The use of the obtained $\delta^{18}O$–δ^2H data of pit lake waters and surrounding groundwaters allow to make precise mass balance calculations and hydrodynamic models which are essential to define the influence of groundwater on the lake hydrodynamics. Sulfur isotopes ($\delta^{34}S$) of dissolved sulfate and associated sulfate solids have been also widely used in environmental studies of mine-impacted waters and AMD (e.g., Taylor and Wheeler, 1994; Seal et al., 2000; Seal, 2003; Nordstrom et al., 2007). Sulfur isotopic studies have been applied to study the biogeochemical cycling of S (e.g., bacterial sulfate reduction and/or sulfide mineral oxidation), usually in combination with $\delta^{18}O_{SO4}$ analyses, but also to discriminate among different possible sulfur sources and to quantify, through mass balance approaches, mixing proportions of waters with distinct sulfur isotopic signature (Seal et al., 2000; Seal, 2003; Gammons et al., 2009; Matthies et al., 2012).

This study applies isotopic, hydrogeochemical, limnometric and meteorological tools in Cueva de la Mora, an acidic, meromictic, and strongly stratified pit lake of the IPB. The main goal of our work was to improve our understanding of the flooding history, subsequent limnological evolution and present-day hydrological dynamics of complex pit lake-underground mine systems with lacking historical records and with no available monitoring wells. We firstly deduce a flooding model based on tritium abundance of pit lake waters at different depths, and then we investigate the influence of different water inputs (precipitation, runoff, interflow, groundwater) in the present-day water balance of the pit lake. The lake hydrology has been studied by a combination of $\delta^{18}O$ and δ^2H isotopes with continuous monitoring of lake volume, water composition and weather data series. This combined approach may be useful in many other pit lakes with associated underground mining and where hydrogeological studies are frequently very limited or unavailable. The results presented in this study can be helpful in the design of future mine closure plans in open pit excavations with intersecting galleries, as well as in the evaluation of future remediation attempts.

2. Site description

2.1. Mine history and design

The pit lake of Cueva de la Mora is situated at the north of the province of Huelva, in SW Spain. The deposit of Cueva de la Mora was mined by both underground and open-cast workings from 1875 to 1971. The mine was abandoned and flooded in the late 1940s, dewatered and re-opened at some moment during the 1950s and 1960s, and finally abandoned in 1971 (AZSA, *unpublished report*). After the cessation of pumping operations, the mine galleries, shafts and open pit were progressively flooded, although the duration and technical details of the flooding process remain unknown. The former pit presently holds a small lake with surface area of 17,600 m^2, maximum depth of 38–40 m, and volume around 282,000 m^3. The lake shows an elongated geometry with an E–W direction (Fig. 1A). A re-vegetated pile with surface area around 58,700 m^2 and containing waste-rock materials from the pit excavation, is situated immediately north of the mine pit. A bathymetric map of the pit lake, along with a cross-section of the entire mine-pit lake system, is given in Fig. 1. Panoramic views of the lake are also shown in the Supplemental material (SP1).

The former mine included three main shafts (Pozo San Alberto, Pozo Enrique and Pozo Santa Bárbara) located at only a few meters to the East, North and West of the mine pit, respectively (Fig. 1a). A 3D digital model of the mine has been developed on the basis of old mine maps and sections and reveals a dense network of sub-horizontal galleries situated in different levels (Fig. 1b). Many of these galleries included rooms of variable size. The galleries were connected with the former pit in at least three different levels (54, 64 and 76 m; Fig. 1b), which roughly correspond to water depths of 13, 25 and 40 m in the pit lake. Some small ventilation shafts also connected the pit bottom with the underground mine galleries situated below.

2.2. Mine hydrology

The host rocks of the massive sulfide mineralization are mostly volcanic rocks (e.g., tuffs and lava flows of rhyolitic to dacitic composition; Sánchez-España et al., 2002). These lithologies have a very low porosity and a relatively low hydraulic permeability limited to the existing joints and fractures. However, at the time of active exploitation this mine had a significant groundwater input, with recharge rates of 3.5 L/s in summer and 17.5 L/s in winter