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The role of surface water and mine groundwater in the chemical stratification of an acidic pit lake (Iberian Pyrite Belt, Spain)

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SUMMARY

The hydraulic system of the Concepción mine is made up of an open pit and an underground mine, which are currently flooded and hydraulically connected. The Concepción pit lake has shown permanent chemical stratification (meromictic lake), where two layers with different density and chemical composition can be differentiated: (i) a thick superficial layer of 11 ± 2 m deep, with a low concentration of dissolved solids (mixolimnion) and (ii) a thin bottom layer from 11 ± 2 m to 16 m deep (monimolimnion), exhibiting vertical changes in its physico-chemical parameters, with decreasing redox potential and increasing T, pH and dissolved solids content with depth. The distribution of the Concepción pit lake layers depends on recharge processes and the loss of water from the system. In winter, rainfall and runoff result in a rapid increase of lake levels. The lake regains its initial level whenever water is lost through an old mine adit, since galleries and shafts act as preferential pathways for inflowing and outflowing water. This network is connected to the bottom of the lake, resulting in the progressive downward movement of the chemocline. Furthermore, runoff generates a less dense superficial layer, which triggers the development of an ephemeral chemocline in the mixolimnion. In summer, the mixolimnion loses water by evaporation which is partially compensated by groundwater inflowing from the lake bottom, resulting in the upward movement of the permanent chemocline. During this period the water level in the system is below the outlet level, which therefore renders the outflow of water inactive. During this stage, the mixolimnion remains homogeneous and the shallow chemocline disappears. Taking into consideration the hydrochemical characteristics of this pit lake and the spatial distribution of the layers identified, a model that explains its seasonal limnological evolution is presented.

1. Introduction

Numerous mines that are located along the Iberian Pyrite Belt (IPB) have been exploited both as open pit and underground mines, an aspect that favors hydraulic connection between both systems after flooding. The latter event takes place after pumping ceases, which depresses the piezometric level during periods of mineral extraction.

At present, the Spanish side of the IPB is host to over 30 mine pits that are the result of massive sulfide mining activities. These pits are generally abandoned since no mineral extraction activities (with the exception of Las Cruces) or maintenance activities aimed at preventing flooding are currently taking place, which have resulted in the formation of pit lakes (Lopez-Pamo et al., 2009). Generally, lakes along the IPB are acidic (pH 2–3) with high concentrations of sulfates and metals (Fe, Zn, Cu, Co and Ni) due to the oxidative dissolution of pyrite and other sulfides along with other elements (Al and Mg) that are generated from the dissolution of aluminosilicates in an acidic medium present in the host rock. The size and depth of the lakes are highly variable, depending on the dimensions of the pits and their degree of flooding. Some lakes can reach 100 m depth but most of them show depths between 25 and 50 m.

Eighty-five percentage of mine lakes in the IPB are meromictic (i.e., they exhibit permanent chemical stratification) while the remaining 15% are holomictic (involving a mixing process during the winter that results in the homogenization of lake water). Thermal stratification occurs in all lakes from the beginning of spring through the end of fall. Summer thermal stratification in meromictic lakes increases the intensity of its overall stratification, therefore enhancing the stability of its water column (Sánchez-España et al., 2008; Lopez-Pamo et al., 2009). Several studies have established a relationship between lakes that have low depths and holomictic lakes, as this aspect favors mixing processes during the winter (Levy et al., 1997; Wetzel, 2001). Nonetheless, depth is not the only determining factor known to govern the development of holomixis in lakes (Boehrer and Schultze, 2008). Despite its shallowness, previ-

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ous studies have confirmed that Concepción Lake is a meromictic lake (Lopez-Pamo et al., 2009) since it displays a monimolimnion that occupies the lower third of its water column.

Several works have recently been published which describe the hydrochemistry of the water column in these pit lakes and the limnological processes taking place therein (Santofimia et al., 2007a, 2007b, 2012; Sánchez-España et al., 2008, 2009, 2013; Lopez-Pamo et al., 2009; Díez Ercilla et al., 2009). Despite the build-up of this knowledge, the study of the factors influencing the development of holomixis or meromixis in lakes is far from exhaustive.

The objective of this work is to understand why a pit lake with low depth (16 m) displays a permanent chemical stratification of certain intensity while hosting one of the mixolimnions carrying the lowest amount of dissolved solids in the entire IPB.

2. Study site

The Concepción mine, located in the northeast of Huelva province (Iberian Pyrite Belt, Spain) was exploited by underground and opencast mining from 1853 to 1986. Underground mining activities began in 1853 (two floors) using room and pillar methods, reaching a depth of 13 m via opencast mining. In 1874, the opencast exploitation reached the 6th level of the underground mine by means of five banks (Fig. 1). Water was extracted through a tunnel by gravity, which was connected to the 9th floor and had its exit close to Odiel River (Pinedo Vara, 1963) (Fig. 1). Groundwater generated between the 9th and 12th floors was pumped toward this tunnel (ca. 35,000 m^3/year). The mine was abandoned in 1986. The tunnel was sealed in the 1990s and caused flooding in the underground mine. The flooding reached the base of the mine pit at a later date 1993 (Checa et al., 2000).

The pit was excavated in a streambed and receives runoff from a basin with a surface area of 0.39 km^2. The system comprises the underground mine (shafts and galleries) and the mining pit, which is at present flooded and connected hydraulically (Fig. 1). The pit lake is 280 m long, 60 m wide (equaling a total area 12,000 m^2) and has a maximum depth of 16 m. The area of maximum depth is located at the west of lake (Fig. 2).

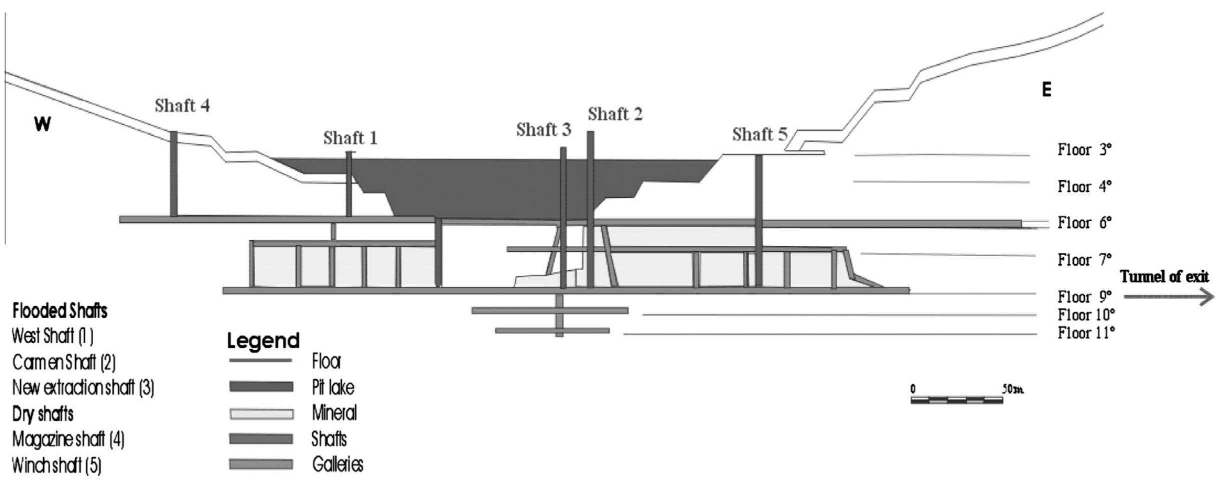

Fig. 1. Sketch depicting underground and opencast mining in Concepción mine. Diagram adapted by Pinedo Vara (1963).

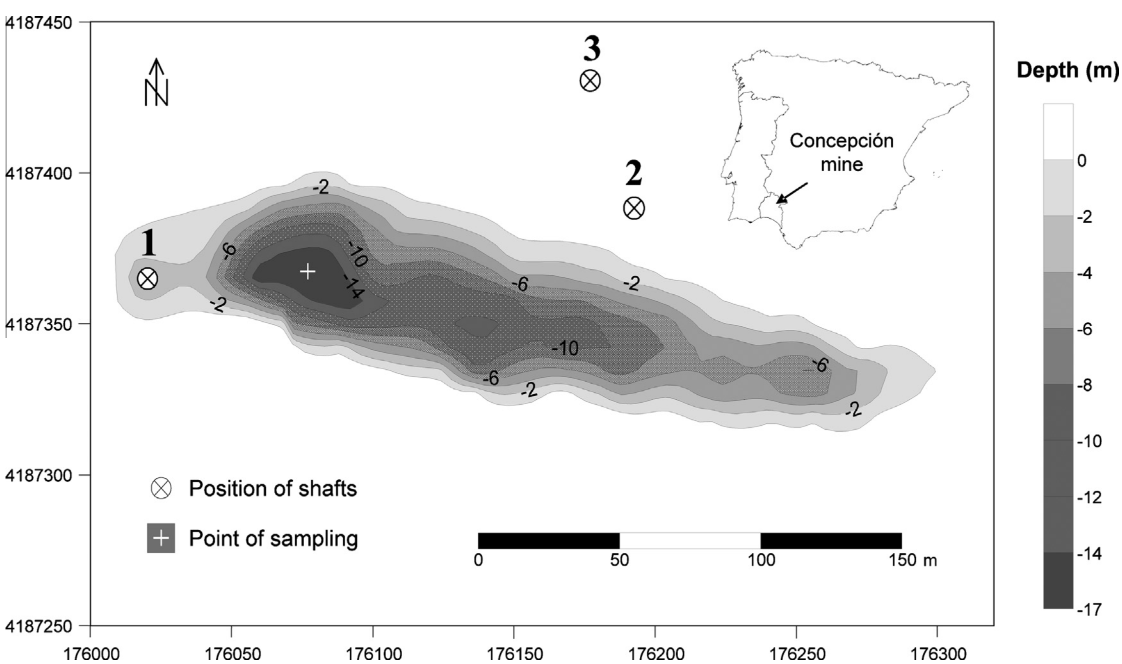

Fig. 2. Geographical location and bathymetric map of the mine lake at Concepción mine.

The lake level and the water level in the shafts are regulated by an exit through a mine adit (spring), which is located to the north of the pit lake and is a source of acid mine drainage (AMD). Recent research has revealed the presence of permanent discharges that flow from several abandoned mines into the Odiel River, which is a natural river located very close to mine. The first discharge is from Concepción mine and transfers significant amounts of acid and dissolved metals to the Odiel. During the study, the flowrate of this AMD was of 14 L/s, with the following physico-chemical characteristics: pH 3.0, EC 1.6 mS/cm, SO_4 1012 mg/L, Fe 127 mg/L, Al 61 mg/L, Zn 3.8 mg/L, Cu 4.2 mg/L and Co 0.5 mg/L (data not published).

Generally, the sources of water inflows that flood mining pits include groundwater, rainfall and runoff, which favor the oxidative dissolution of pyrite and the subsequent acidification of water, along with the concomitant dissolution of other sulfides (e.g. chalcopyrite, sphalerite, galena, arsenopyrite), hydrated metal sulfates (e.g. epsomite, hexahydrite, copiapite, halotrichite, tetrahedrite–tennantite) and gangue aluminosilicates (e.g. feldspars, chlorite, sericite) from the country rocks. As a result, the pit lake that developed in this mine is acidic (pH ~3), as in the case of the majority of the mining lakes of the Iberian Pyrite Belt but, unlike the rest, presents low concentrations of sulfate and metals (Fe, Al, Cu, Mn, Zn, Co) (Lopez-Pamo et al., 2009). Mine groundwater chemistry can be studied through three mining shafts. Shaft 1 is located inside of the pit lake to its west (Fig. 2). Shaft 2 is located in the pit slope and shaft 3 is located outside of the mine. Both shafts are flooded (Figs. 1 and 2) and the maximum depth of the water columns in the shafts is between 13 and 18 m.

3. Material and methods

3.1. Field measurements and sampling

Field and analytical data correspond to several sampling events between November 2008 and February 2011. Depth measurements and vertical profiles of pH, redox potential (Eh), temperature (T), dissolved oxygen (DO), electric conductivity (EC), turbidity, photosynthetically active radiation (PAR) and chlorophyll-a concentration were collected using a Hydrolab® Datasonde S5 probe from

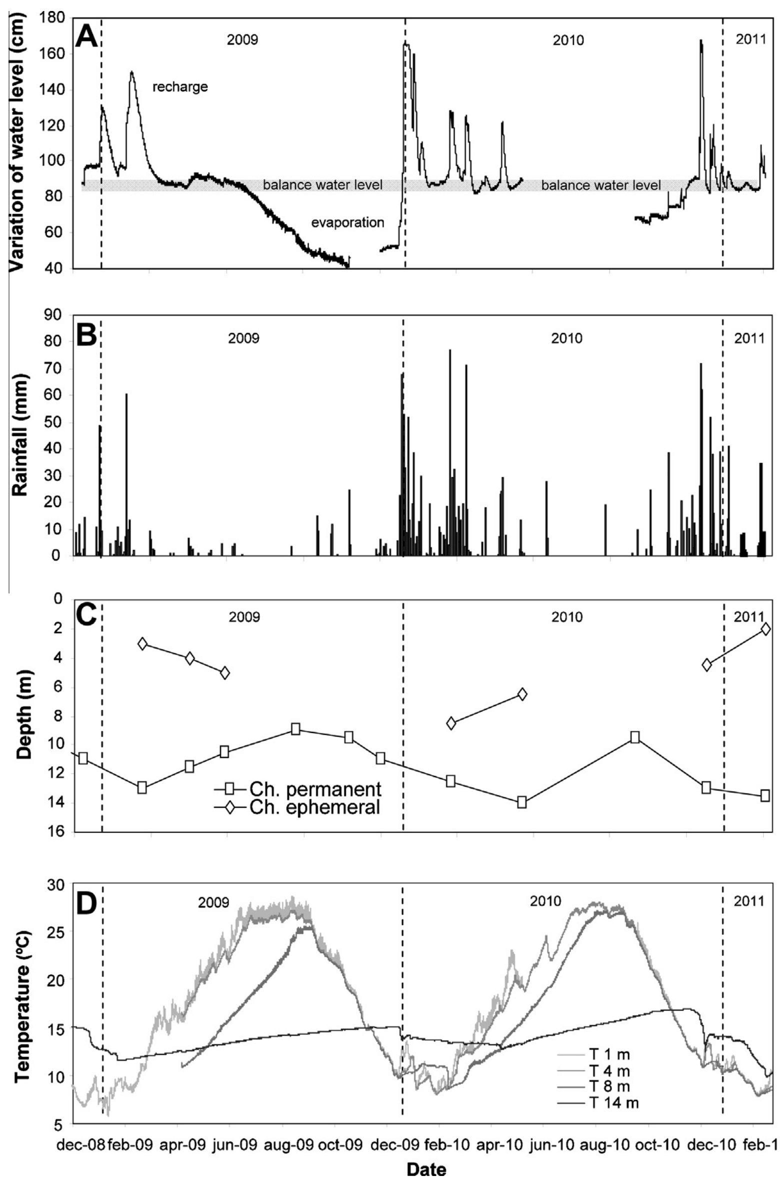

Fig. 3. Study period showing (A) relative variation of the water level, (B) daily rainfall, (C) time evolution of chemoclines (Ch.) at depth and (D) temperature log in the pit lake at 1, 4, 8 and 14 m depth.

Hach Company. Lake data at different depths were collected from the surface to the deepest point. Additionally, depth measurements and vertical pH, Eh, T, DO and EC profiles were taken in three shafts using a Hydrolab® Quanta probe.

The concentration of Fe(II) was measured by reflectance photometry with a Merck RQflex10 reflectometer and Reflectoquant® analytical strips. Two different reagents were used depending on the Fe(II) concentration: (1) Ferrospectral® for the 0.5–20 mg/L range, and (2) 2.2′-bipiridine for the 20–200 mg/L range. A number of samples had to be previously diluted with acidified distilled water, since the value fell outside the range that is measurable by this analytical equipment. The addition of a reducing agent (ascorbic acid) was required to determine total iron concentration. Bathymetric measurements were obtained using a Garmin Fishfinder Probe model 160C and a Garmin GPS model 76S running in differential mode. The information was processed using Surfer 8 software and isobaths were obtained by interpolation of points.

Changes in water level during the study were measured using Cera-Diver and Baro-Diver sensors (from Van Essen Instruments) to compensate for barometric pressure data. Water temperature was recorded at hourly intervals at 1, 4, 8 and 14 m depths using a Cera-Diver sensor and Hobo® Pro v2 instrument. Daily rainfall data were obtained from El Campillo weather station located 20 km to the southeast. This station is managed by the Andalusian Regional Government and is the most representative of this area.

Lake water samples were collected with an opaque, 2.2 L-capacity, BetaPlus® PVC bottle from Wildlife Supply Company®. Depths sampled in the lake can differ as a function of vertical profiles. All samples were filtered on site with 0.45 μm membrane filters from Millipore, stored in 125 mL polyethylene bottles, acidified with HNO_3 and refrigerated at 4 °C during transport.

3.2. Laboratory analyses

Water samples were analyzed using Atomic Absorption Spectrophotometry (AAS, Varian SpectrAA 220 FS equipment) for Na, K, Mg, Ca, Fe, Cu, Mn, Zn and Al, Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, VarianVista MPX equipment) for Ni and S, and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Leco Renaissance) for Cr, Mn, Co, Cd, Th, and U. Sulfate was gravimetrically measured as $BaSO_4$. The accuracy of the analytical methods was verified against certified reference waters (TM-27.3 and TMDA-51.3 of National Water Research Institute) and close agreement with certified values was achieved for all metals. ^{115}In was used as an internal standard for the calibration and measurement of ICP-MS determinations.

4. Results and discussion

4.1. Hydrologic (recharge and evaporation in the pit lake)

The average annual precipitation during the period 2001–2010 was 715 mm (El Campillo, weather station; CAP-JA, 2011). Precipitation values in 2008 and 2009 approach this value (691 mm and 737 mm respectively), which means that these years can be considered as normal. Nonetheless, precipitation in 2010 reached 1380 mm, representing a very high value that almost doubles the average value.

The maximum lake level oscillation during the study period (November 2008/February 2011) was 1.2 m. Also during this period the lake displayed a constant equilibrium level (Fig. 3A). High precipitation in 2010 (Fig. 3B) was reflected in the number and intensity of positive lake level oscillations but not in its equilibrium level. The level in the lake rose quickly during episodes of high precipitation and dropped until reaching its usual level as soon as precipitation ceased (Fig. 3A). During summer, when temperatures are high and no precipitation occurs, the lake level dropped slowly and progressively due to evaporation, moving away from the equilibrium level (Fig. 3A). The greatest lake level increase above its usual level was of +0.8 m and occurred in December 2009 and 2010. The greatest decrease equaled −0.4 m at the end of the summer of 2009. After intense precipitation, the lake/groundwater system recovers its equilibrium level, discharging water through an old, partially sunk gallery which is located 115 m to the north of the lake. Between the lake and the location of the mine adit there are two shafts: shaft 2, located very near to the lake (10 m) and shaft 3, which is equidistant between both (Fig. 2). The physico-chemical nature of the upwelled water (pH, EC, DO, Fe(II), Eh) that reaches the surface through the gallery resembles more the groundwater that floods the shafts than lake water, as observed on several occasions. Therefore, it can be concluded that the system is recharged mainly by runoff water from the basin and, to a lesser extent, by direct precipitation falling on the lake, and becomes re-balanced through the loss of groundwater that floods the underground mine.

Taking into account the episodes of lake level increase in January and February 2009 and April 2010, after which precipitation ceased completely until the equilibrium level was restored, it is possible to shed some light on the manner in which water is lost from the lake/groundwater system.

In January 2009, 83 mm of rainfall in 4 days resulted in a lake level increase of 31 cm (Fig. 3A and B), which equals an increase in volume of 3700 m^3. The level that existed prior to rainfall was restored in 14 days, meaning the average discharge of water lost from the system was 260 m^3/day (3.0 L/s). If it is considered that this discharge was also lost during the days ($n = 4$) when the lake level rose during precipitation, the total volume of water that would have entered the pit equals 4800 m^3.

During the February 2009 episode, 95 mm of rainfall in 6 days resulted in a lake level increase of 53 cm (Fig. 3A and B), which equals a volume increase of 6400 m^3. After 20 days, the equilibrium level was restored, indicating that the discharge of water lost equals 320 m^3/day (3.7 L/s). When considering that this loss of water also took place during the 7 days when the level was increasing, the volume of water that reached the lake equals 8600 m^3.

In April 2010 after a winter season characterized by high precipitation (986 mm from December 2009 to March 2010), a recorded rainfall of 99 mm over a 5-day period increased the level by 34 cm (Fig. 3A and B), resulting in an increase of the vol-

Table 1
Water chemistry in Concepción pit lake, mine groundwater in shafts and mine adit, from which water is lost from the system. Data of February 2011.

Sample	SO_4^{2-} (mg/L)	PO_4^{3-} (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Al (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)	Co (mg/L)	Pb (mg/L)	Ni (mg/L)
Mixolimnion	210	0.07	8.3	1.3	16.6	16.3	9.5	1.5	7.4	1.36	2.3	0.13	0.05	0.02
Monimolimnion	2742	0.18	15.8	3.1	137	77.6	120	16.9	861	21.7	42.6	1.66	0.31	0.26
Shaft 1	1214	0.14	17.3	1.84	80.6	60.9	35.1	4.78	332	10.4	22.2	0.72	0.05	0.09
Shaft 2	1906	0.17	11.0	1.56	103	49.8	80.3	12.0	560	17.8	40.0	1.17	0.11	0.12
Shaft 3	2676	0.31	12.4	1.66	145	63.3	112	17.0	696	23.8	49.7	1.71	0.10	0.20
Adit	1876	0.17	11.4	1.88	108	49.8	86.6	12.0	559	18.0	40.6	1.19	0.11	0.12

ume in the lake equal to 4100 m^3. The initial lake level was restored 7 days after precipitation ceased. In this occasion, the lost water discharge was greater (585 m^3/day; 6.8 L/s), probably due to the degree of saturation of the ground after a winter with high rainfall. Continuing with the rationale presented earlier, the total volume of water entering the lake can be estimated to be 7000 m^3.

During visits conducted when the lake level was above its equilibrium level (February 2009, 2010 and 2011), it was confirmed that the volume of water lost from the lake/groundwater system via upwelling through the partially subsided gallery was within the range of discharged flowrates calculated for each of the three aforementioned events (3–7 L/s). Furthermore, in February 2011, it was also confirmed that the chemistry of upwelled water and water in shafts 2 was very similar, and that it clearly differed from the water chemistry found in shafts 1 and 3 and in the lake (Table 1). This indicates that the upwelling water comes exclusively from this section of the underground mine.

In the three aforementioned episodes, water recharge to the lake was 15%, 22% and 17% respectively of the total rainfall collected in the basin. This represents a supply of water equal to 7–12% of the total volume of the lake when it is at its usual level. During the period between June and August 2009, the level of the lake dropped 41 cm (4.5 mm/day), which represents a volume loss of 4900 m^3 (53 m^3/day). Based on net evaporation data of the free water surface (CHG, 2011), values in the lake would equal 54 cm, which is somewhat higher (20%) than the actual lake level drop during this period (41 cm). The difference between the actual drop in the lake level and the drop corresponding to the net theoretical evaporation could be due to the inflow of groundwater into the lake, which represents a supply of water that must take place preferentially through the galleries of level 6 that reach the deepest part of the pit (Fig. 1).

4.2. Meromixis: mine groundwater vs. surface water

Concepción lake is always chemically stratified, meaning it is a meromictic lake. Two layers of distinct nature can be differentiated in the water column: (1) a mixolimnion, which is an acidic (pH 2.5–3.2), dissolved oxygen rich (7–11 mg/L) superficial layer located at 11 ± 2 m depth with moderate quantities of dissolved solids (EC 0.5–2 mS/cm) overlying and (2) a monimolimnion, which is a thin anoxic and acidic (pH 2.5–4) layer located at the bottom, displaying increasing temperature and dissolved solids content (EC 2–6 mS/cm) with depth (Figs. 4 and 5).

In this mine, the hydraulic system consists of the flooded mining pit (lake), which acts as a reservoir that receives surface water, and the flooded underground mine, whose galleries are connected to the deepest zone of the pit (Fig. 1). The Concepción pit is the meeting place of surface water and groundwater coming from the underground mine. This situation causes the permanent chemical stratification observed in the lake. A similar situation was observed in other pit lakes, such as the Island Copper pit lake in British Columbia (Fisher and Lawrence, 2000) and Lake Goitsche in Germany (Boehrer et al., 2003), which were particularly sensitive to the involvement of these two types of waters in the development of their meromixis. The development of meromixis is normally favored in lakes that have high relative depth (Doyle and Runnells, 1997), although other very shallow meromictic lakes exhibiting narrow and isolated deeper basins were also studied (Bachmann et al., 2001; Seebach et al., 2008; von Rohden et al., 2009b). This basin is host to a number of processes that favor the

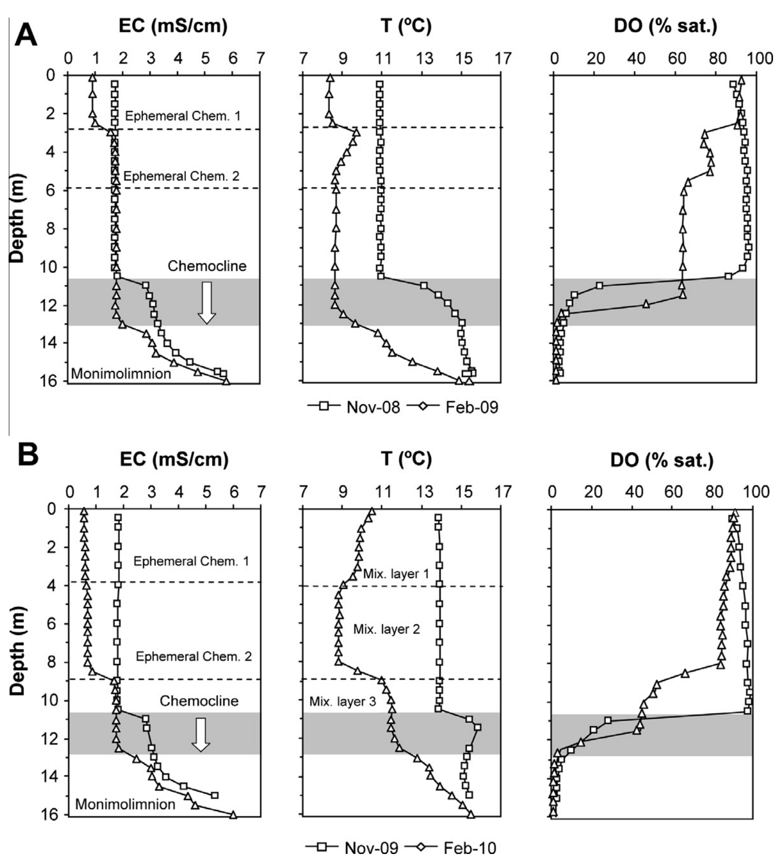

Fig. 4. Vertical electric conductivity (EC), temperature (T) and dissolved oxygen (DO) profiles as a function of depth during winters of the study period (A) 2008/2009 and (B) 2009/2010. Chem. chemocline. Mix. Mixolimnion.

creation of a layer that has greater density, which is also protected from mixing processes that take place in the rest of the lake. Concepción lake has this type of basin. Depths greater than 11 m, (which is the average depth at which the monimolimnion develops) exist only in a small section of the lake that is equivalent to 15% of the total surface, forming a basin that has depths of 16 m (Fig. 2). The warming and enriching of dissolved solids that has place in the monimolimnion (Figs. 4 and 5) must have its origins in the supply of groundwater from the underground mine. This water usually shows high EC (4–5.5 mS/cm; Fig. 6B and C) due to the washing of galleries and tunnels whose walls often contain sulfides and hydrated metal sulfates. The dissolution of the latter is particularly significant in the first stages of flooding of the galleries, as they are highly soluble and quickly release metals, acidity and sulfates to the medium (Nordstrom, 1982; Cravotta, 1994; Bowell and Parshley, 2005). The exothermic character associated with the oxidation of pyrite (Nordstrom and Alpers, 1999; Schimmele and Herzsprung, 2000) and the dissolution of hydrated metal sulfates (Nordstrom and Alpers, 1999) may explain the warming of the water. During the study, shafts showed *T* values in the range of 15–18 °C (Fig. 6), which match with the *T* range measured at the bottom of the pit (Fig. 5). It must not be discarded however that the deepest part of the lake is also influenced by a heat flux coming from sediments (von Rohden et al., 2010), since some anaerobic reactions taking place therein are also exothermic in nature.

A gradual increase in T and EC with depth can be found in lakes where the double-diffusion convection phenomenon takes place (von Rohden et al., 2010; and references therein). However, in the case of Concepción lake, the formation of micro-layers showing similar T and EC values (which is very characteristic of this phenomenon) was not observed; this may be due to the scale of observation used, with intervals of 0.5 m between contiguous measurements which is insufficient to detect the existence of these micro-layers (Schmid et al., 2004; Schmid and Wüest, 2005; von Rohden et al., 2009a, 2010). The chemical characteristics of the deepest water in the lake are similar to that of groundwater in shafts 2 and 3. With the exception of its most superficial part (up to 3 m depth), water in shafts 2 and 3 is anoxic, with EC values ranging between 4.2 and 5.5 mS/cm (values that are similar to those found at the bottom of the lake) and iron content in the form of Fe(II), as in the case of the monimolimnion. Shaft 1, which is submerged in the lake at a depth of 1.5 m (Fig. 2) is a mix of lake water (mixolimnion) and mine groundwater, which differentiates it from the monimolimnion (Table 1 and Fig. 6A).

Normally, groundwater recharge in pit lakes is usually more important than surface water recharge when compared with natural lakes (Atkins et al., 1997). In Concepción lake, the inflow of surface water is more important than the inflow of groundwater, as will be shown next, but both are essential for determining lake stratification.

4.3. Vertical fluctuation of the chemocline

The chemocline is the transition zone that separates the mixolimnion from the monimolimnion. During the study period, the chemocline oscillated between 9 and 14 m depth. The variation of the chemocline with depth follows a clear seasonal cycle (Fig. 3C). The chemocline is located at a greater depth in the winter–spring transition months after the rainy period. The chemocline is found at a lower depth at the end of the summer, just before the first rains of the fall (Fig. 3B and C). During the winter, two remarkable processes take place which can favor the down-

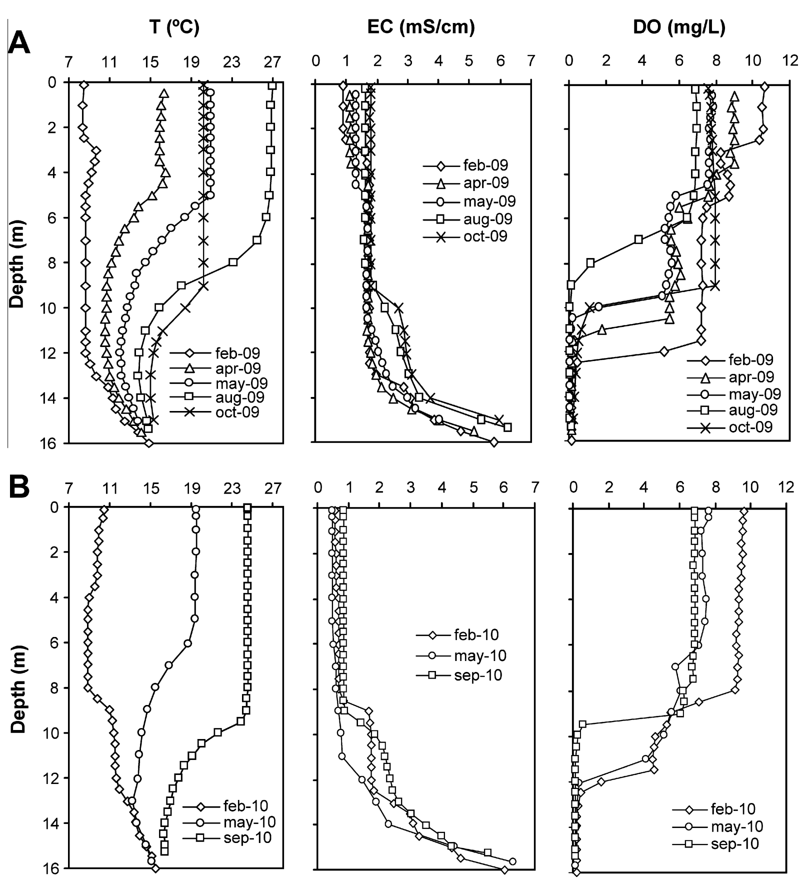

Fig. 5. Vertical temperature (T), electric conductivity (EC) and dissolved oxygen (DO) profiles as a function of depth. Study period from 2009 to 2010.

ward movement of the chemocline: (1) the cooling of the mixolimnion, which erodes the chemocline and (2) the inflow of runoff into the lake during the rainy season, which thickens the mixolimnion (see Section 4.1).

The first process favors the activation of winter mixing, which leads to the homogenization of the mixolimnion. Annual mixing was recorded continuously using T recorders placed at 1, 4 and 8 m depth (Fig. 3D) and discretely in vertical profiles (using a multi-parameter probe) during the months of November of 2008 and 2009 (Fig. 4). In this time of the year, T and EC show invariable values from the surface to the chemocline, indicating therefore that the mixolimnion is a homogeneous layer. The progressive density increase observed in the mixolimnion due to continuous cooling of the lake (Fig. 3D) gradually erodes the chemocline. This phenomenon becomes evident when studying October and November 2009 data, where a 1.5 m drop of the chemocline was recorded (Fig. 3C) in a period when rainfall was practically inexistent (Fig. 3B). This indicates that the drop of the chemocline can be exclusively attributed to cooling and the subsequent destabilization of the mixolimnion. The erosive lowering of the chemocline due to seasonal mixing has been described in other pit lakes (e.g. von Rohden and Ilmberger, 2001). Other parameters also point to the fact that the convective mixing of the mixolimnion may end up eroding the chemocline. For example, in some winter months, turbidity was detected in the most superficial part of the monimolimnion (data not shown), which may be due to the precipitation of Fe(III) that formed after the oxidation of abundant Fe(II) present in the monimolimnion, the latter process being favored by the supply of dissolved oxygen from the mixolimnion.

With respect to the second process, it must also be mentioned that the inflow of fresh water into the lake (mixolimnion) in the form of runoff (see Section 4.1) also favors the downward movement of the chemocline. This has been explained by Castendyk and Webster-Brown (2007) in their conceptual limnological evolu-

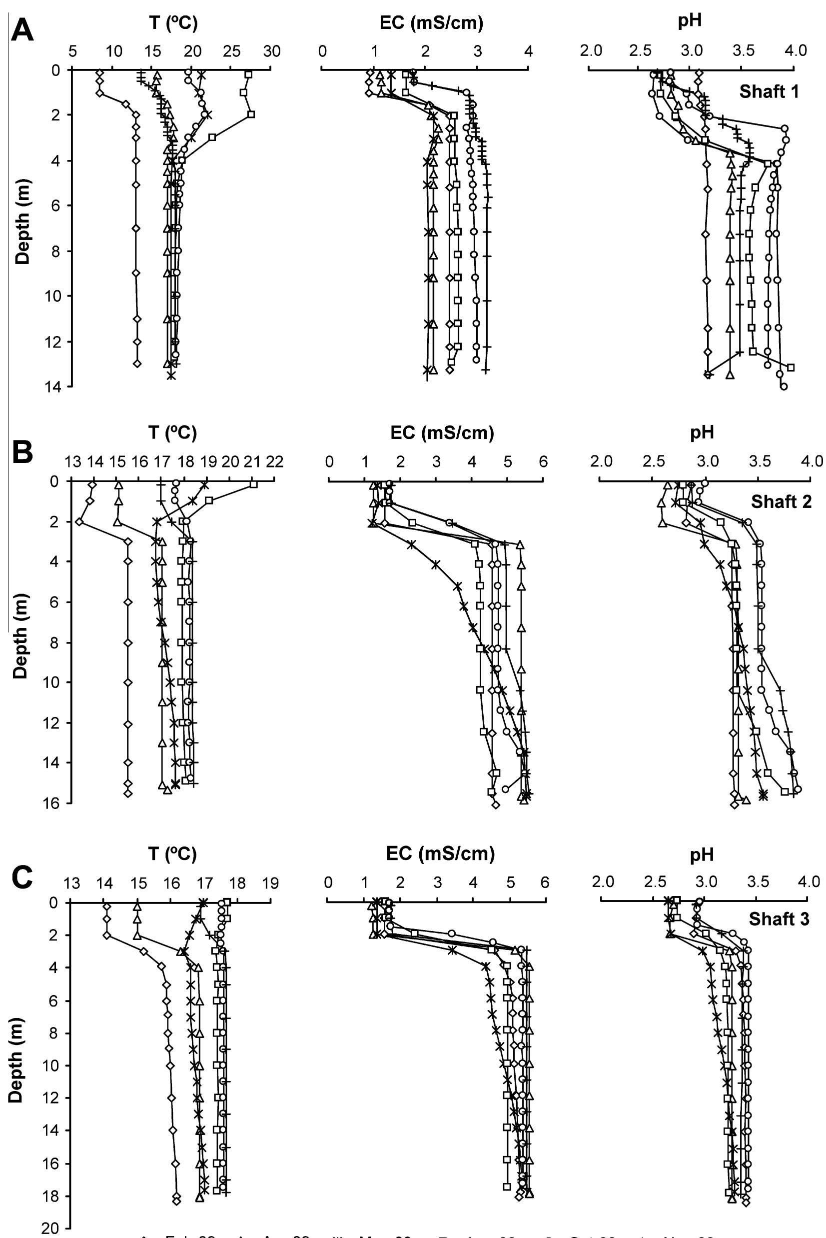

Fig. 6. Vertical temperature (T), electric conductivity (EC) and dissolved oxygen (DO) profiles as a function of depth in (A) shaft 1, (B) shaft 2 and (C) shaft 3. Data from February to November 2009.

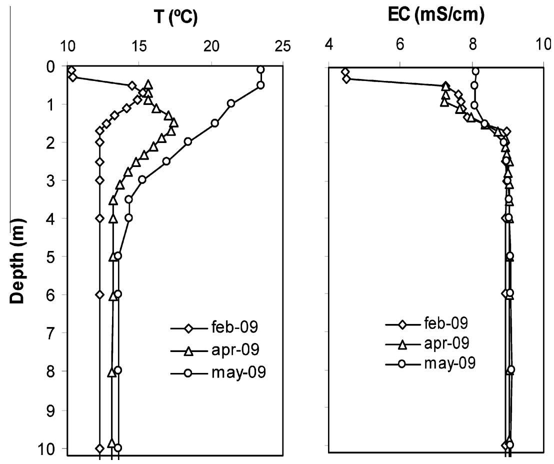

Fig. 7. Vertical profiles showing variations in temperature (T) and electric conductivity (EC) as a function of depth in the Nuestra Señora del Carmen pit lake. Only the ten first meters are shown, as the values between 10 and 35 m depth are similar. Graph modified from Santofimia et al. (2012).

tion model of a meromictic lake formed by ground and surface water. According to these authors, during periods of rainfall and when the amount of surface water exceeds groundwater recharge, the mixolimnion thickens and the level of the lake rises, surpassing the piezometric level, an event that favors the release of water from the lake to the surrounding rock substrate. The opposite situation occurs during the dry season, where the supply of groundwater that is denser than the lake, coupled with losses due to evaporation of the superficial layer causes the chemocline to move toward lower depths.

In the case of Concepción lake, when the pit receives high surface water inflow, such volume results in an increase in the lake level (Fig. 3A). The system then tends to recover its equilibrium level by expelling groundwater flooding the underground mine through an old mine adit. The system recovers its equilibrium level in just a few days after rainfall stops (Fig. 3A). The lake/flooded underground mine combination behaves like a system of communicating vessels. The system gains water (runoff, rainfall) or loses water (evaporation) through one of such vessels (pit-lake), while water is lost through the other vessel (mine adit) whenever the lake exceeds its equilibrium level. The differing nature of the water in the lake (mixolimnion) and groundwater (monimolimnion) makes these waters relatively immiscible, which is the reason why their contact surface (the chemocline) moves along the vertical.

The supply of water to the lake in the wet season causes the chemocline to drop between 1.5 and 2.5 m (Fig. 3C). 2010 witnessed the greatest drop of the chemocline due to abundant precipitation (Fig. 3B). When considering the inflow of water to the lake during the period December-09 and May-10 (30,000 m^3) as an example, this must imply a drop of the depth to the chemocline equal to approximately 2.2 m (Fig. 2). At the beginning of this period, the chemocline was located at 11 m depth, reaching 14 m at the end (Fig. 3C). When considering the rise in the level of water in the lake, the actual drop in the elevation of the chemocline was of approximately 2.7 m (Fig. 3C). It must also be noted that from December-09 to February-10 the mixolimnion experienced slight cooling which may have triggered a certain degree of erosion of the chemocline (Fig. 3D).

Observations have verified the upward movement of the chemocline during the summer. The chemocline even rose to approximately 9 m depth during the summer of 2009 and 2010. A progressive drop of the level in the lake occurs due to evaporation during periods of low water level (Fig. 3A). This situation causes the elevation of the lake level to remain below the piezometric level, which favors groundwater recharge (Castendyk and Webster-Brown, 2007). The loss of water from the mixolimnion is partially compensated by groundwater recharge from underground mine, thus favoring the upward movement of the chemocline and the thickening of the monimolimnion.

Therefore and as an example, from May 27th to August 18th 2009 the chemocline went from 10.5 to 9 m depth. Since during that time interval the level in the lake dropped 32 cm, this represents a real rise in elevation of the chemocline of approximately 1.2 m (Fig. 3). In the following summer, from May 12th to September 22th, the chemocline rose from 11.5 m to 9.5 m depth; since the level in the lake dropped 20 cm, this equals an real elevation of the chemocline of approximately 1.8 m. This seasonal movement of the chemocline was observed at other pit lakes, such as the Island Copper pit lake in British Columbia (Fisher, 2002), Dexter pit lake in Nevada (Balistrieri et al., 2006), Moritzteich Lake and Wadsee pit lake, both in Lusatia, Germany (von Rohden et al., 2010). In the latter, seasonal behavior is the opposite of what has been described in this section. Upward movements were recorded in the winter in the presence of high groundwater inflow and at a time when the inflow of surface water was quantitatively negligible.

4.4. Mixolimnion evolution

In the fall, the mixolimnion becomes an oxygen-saturated chemically and thermally homogeneous water layer that reaches an approximate depth of 11 m (Fig. 4). After the rainfall in the winter, the mixolimnion displayed chemical stratification as a result of dilution that is generated by the supply of fresh water (Fig. 4). Such dilution of the water that is located closer to the surface of the lake creates a lighter superficial layer (with lower EC), which floats over the rest of the mixolimnion, leading to the formation of a (ephemeral) chemocline within. This process can take place more than once during the winter, meaning that more than one chemocline will form in addition to multiple water layers in the mixolimnion (Fig. 4). Therefore, direct precipitation on the lake and runoff during the winter favor the formation of a multilayer mixolimnion, where the age of each chemocline increases with depth.

At the end of the winters of 2008/09 and 2009/10, the mixolimnion consisted of three water layers that showed an increasing amount of dissolved solids (greater EC) with depth. This chemical stratification limits the capacity of the mixolimnion to develop certain patterns of thermal stratification and its ability to follow a stepped dissolved oxygen saturation gradient whose values decrease with depth (Fig. 4). Winter chemical stratification of the mixolimnion makes the existence of an inverted thermal stratification possible (i.e., the lower layer being warmer than the upper layer), since the density of water is controlled mainly by its EC (dissolved solids content). A maximum local temperature value may develop in association with the shallower chemocline during the lake warming period (February–April 09, Fig. 5A). Relative maximum temperature values associated with chemoclines have been described by von Rohden et al. (2009, 2010) in pit lakes (Waldsee and Moritzteich) in Germany. These authors have identified maximum local temperature values immediately below the chemocline that separates the mixolimnion from the monimolimnion, during the period when the lake undergoes cooling. The authors argue that the latter is due to the low transmission of heat through the chemocline from a still warm monimolimnion to a lower temperature mixolimnion undergoing cooling. This type of maximum local temperature values therefore appears when the chemocline is eroded as its depth increases, due to cooling of the mixolimnion. This type of thermal maximum has been recorded in the lake studied in November-09 (Fig. 4B).

The rationale provided by von Rohden et al. (2009, 2010) does not satisfy the interpretation pertaining to the maximum temperature values that are associated with the more superficial chemocline, since during this period the lake is in the process of warming up. During this period, the T of the superficial layer increased by more than 7 °C, the chemocline dropped by one meter and the lower layer developed a stable thermal gradient. Despite all these changes, the maximum thermal value was preserved immediately below the chemocline (Fig. 5A), which disappeared during the next site visit (May-09). The chemocline continued to be present however, but at a greater depth (ca. 5 m).

Differential warming in the zone where the ephemeral chemocline is present is an active phenomenon, as proven by the increase in temperature of the maximum value by up to 7 °C during this period (February–April 09, Fig 5A). This is in contrast with the maximum local value in the fall, which can be considered to be residual, as no warming exists in the upper zone of the monimolimnion with the exception of some differential cooling of the two water layers that the permanent chemocline puts into contact (Fig. 4).

This phenomenon was identified in another pit lake on the IPB (Nuestra Señora del Carmen mine) (Santofimia et al., 2012). In this case, the chemocline is more intense and is located between 0.5 and 2 m depth; in addition and contrary to the case of Concepción lake, it is also an oxicline whose lower layer is anoxic (Fig. 7). The higher intensity of the chemocline allows for greater warming of the water below it before reaching destabilization. Another example of this phenomenon has been described for the Kaiike meromictic lake in Japan, where a maximum thermal value was identified at 4 m depth located immediately below the chemocline at 2.5 m depth. This coincides with maximum turbidity values due to the abundance of purple sulfur bacteria located at the O_2/S^{2-} limit, where *Chromatium* sp. has also been identified (Oguri et al., 2004). In addition, Wetzel (2001) in fact considers that absorption of solar radiation by a layer of bacteria associated with a chemocline may be the cause of the maximum relative temperature value. There are no signs of high bacterial density at Concepción lake, turbidity is absent and the presence of a redox limit has been ruled out, meaning the maximum temperature value appears to be due exclusively to solar radiation, without the participation of any type of particle.

The work of Ludlam (1996) and references therein mention the frequency with which profiles with maximum thermal values exist in Artic and Antarctic lakes and temperate regions that host chemoclines at low depths. The maximum thermal value is the result of absorption of solar energy in the lower layer which contains greater amounts of dissolved solids and from which the loss of heat by radiation or evaporation is low or eliminated by the less saline upper layer (Cole et al., 1967). Despite thermal inversion, the water column remains stabilized by the increase in density of the lower layer due to its greater dissolved solids concentration. In some of these meromictic lakes located at high altitudes, seasonal warming or cooling of the thermal maximum values was observed, which strengthens the idea of an origin associated with *in situ* solar warming.

This was observed at Concepción lake when the temperature of the lake increases in the spring. In addition, if the ephemeral chemocline is very weak, the maximum thermal value may end up partially destabilizing the water column, triggering a convective process from the thermal maximum up to the surface. This is what appears to be taking place in our lake. The convective process causes the erosion of the ephemeral chemocline, therefore increasing its depth and causing mixing of the more superficial layer with the deepest one, as proven by the evolution of EC values, which increase simultaneously with the drop of the chemocline until equaling those of the lower layer of the mixolimnion (on-going process from February-09, Fig. 5A). The most superficial layer reaches homogeneity since the convective process is active. The process is deactivated as the chemocline increases its depth due to its intensity becoming reduced while the temperature of the upper layer increases.

Thermal stratification (which governs DO distribution) appears as the initial chemical stratification of the mixolimnion disappears. A gradual decrease in temperature and DO was observed in August-09, both disappearing from 6 m to 9 m depth which is where the permanent chemocline is located. This situation became mod-

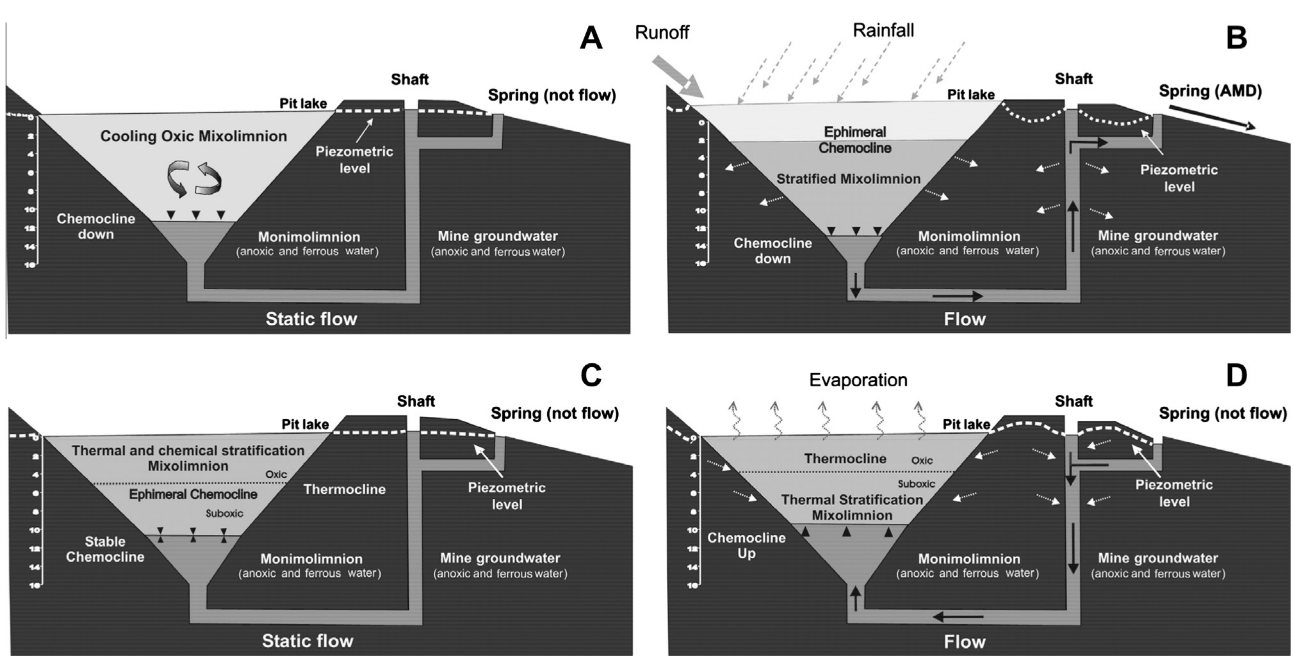

Fig. 8. Conceptual model explaining seasonal limnological evolution in Concepción pit lake. (A) Dry period and mixolimnion cooling, (B) wet period and strong superficial water inflow, (C) dry and spring periods: system in hydraulic equilibrium and (D) dry and summer periods: strong evaporation active in the system.

ified in the fall (October-09), which is when the mixolimnion cools down and tends to become homogenized.

The processes that can generate drops in the oxygen concentration in the different layers making up the mixolimnion may include: the oxidation of pyrite, the oxidation of Fe(III) (e.g. Pellicori et al., 2005; Gammons, 2009), and to a lesser extent, the degradation of organic matter, which is usually scarce in this type of lakes (Ramstedt et al., 2003; Cameron et al., 2006).

4.5. Mine groundwater

The water column in shafts is stratified and is made up of two distinct layers with very different thicknesses and composition (Fig. 6). A thin, 2–3 m thick and lighter (EC 1-2 mS/cm), more acidic (pH 2.5–3) and dissolved oxygen rich superficial layer overlies a lower layer. The latter is thicker (12–15 m), with higher amounts of dissolved solids (EC 4-5.5 mS/cm) and less acidic (pH 3–3.5) and with lower annual thermal fluctuation (Fig. 6). This practically anoxic layer has a redox potential that is characteristic of mine acid water where iron is present fundamentally in the form of Fe(II) (Nordstrom et al., 1979; Grenthe et al., 1992; Nordstrom, 2000), as proven through *in situ* assessments of Fe(II) and total Fe content (data not shown). This type of anoxic acid water that contains most of the iron dissolved in the form of Fe(II) and with low redox potential values (according to its high Fe(II)/Fe(III) ratio) has been described by Pellicori et al. (2005) in flooded shafts in Berkeley mine.

Water in this lower layer is representative of the groundwater that floods the underground mine, especially in shafts 2 and 3 since, as mentioned earlier, the lake floods shaft 1. This layer is usually thermally and chemically homogeneous and does not exhibit T and EC variations (with some exceptions in May-09; Fig. 6) with depth. Occasionally, shaft 2 shows an increase of EC, T and pH starting at 8–10 m depth (Fig. 6B). According to Wolkerdorfer (2008), these variations with depth sometimes coincide with the level in the galleries that reach the shaft.

Water flooding the underground mine shows temporal variations in composition. EC, which is a reliable and stable measurable parameter, is observed to change through the year (Fig. 6). In the shafts, the evolution of EC was observed to display an annual cycle: water is more diluted at the end of the wet season and more concentrated at the end of the dry season (Fig. 6). In addition, its chemistry shows spatial variation: as the distance between the shaft and the lake increases, the concentration of dissolved solids also increases (Figs. 2 and 6). The important temporal variations in the composition of groundwater may be due to an intense and variable flow traveling through the galleries and shafts in the underground mine. The concentration of major ions SO_4 and Fe vary significantly in these shafts. SO_4 concentrations are in the range of 1.8–5.5 g/L in shaft 2, and 2.3–6.5 g/L in shaft 3. The ranges in Fe concentrations are 315–1288 mg/L and 645–1477 mg/L in shafts 2 and 3 respectively. The stark difference in the concentration of a relatively conservative ion such as the SO_4 anion in these waters indicates how far the latter may be from reaching chemical equilibrium.

5. Conceptual limnological model and associated seasonal variations

The hydraulic behavior of the Concepción Pit lake shows certain similarities with the conceptual model proposed by Castendyk and Webster-Brown (2007). In order to be able to apply this model, a number of basic characteristics must be met such as: (i) the most important sources of recharge flowing into the lake must come both from surface water and groundwater; (ii) there must be important differences in density between both types of waters and (iii) the inflow of surface water must show seasonal variability. Concepción pit lake meets all of these characteristics, since its formation is due to both the contribution of surface water (direct precipitation and runoff) and mine groundwater, with strong differences in density between the two. Furthermore, the inflow of surface water displays a seasonal cycle: an important inflow of surface water is associated with higher precipitation during the winter, whereas in the summer this supply practically disappears. An important difference is that, in this case, the hydraulic system (i.e. the lake-flooded underground mine system) remains in hydrological equilibrium, whereby the discharge of water becomes activated whenever a supply of water exists, therefore keeping a constant volume of water in the system. With this initial hypothesis, four stages can be proposed to explain the limnological evolution of the lake as a function of the inflow/outflow of water to/from the system according to seasonal climatic changes and their incidence on the hydraulic gradient (Fig. 8).

Stage 1 represents a dry period that is gradually colder, with the lake at its level of equilibrium. Progressive cooling of the surface of the mixolimnion induces convective processes that homogenize the layer, which take place simultaneously to the partial erosion of the chemocline, causing the latter to move deeper. The exchange of water between the lake and the underground mine must be practically inactive, as the upwelling of water through which the system losses water (Fig. 8A).

Stage 2 corresponds to a cold (winter) period with episodes of high precipitation. Coinciding with these is a considerable inflow of water into the lake, both from direct precipitation and runoff (Fig. 8B). In response to this inflow of water, the level of the lake experiences a rapid rise (Fig. 4A and B), standing above the piezometric level and favoring the discharge of water from hydraulic system. Discharge takes place through an old adit with the galleries and shafts of the underground mine acting as preferred pathways since they are hydraulically connected to the bottom of the pit. Discharge ceases once the equilibrium level in the lake has been attained, and resumes during the next episode of intense precipitation. The fact that a certain amount of water that may be released from the lake into the rock substrate cannot be discarded; nonetheless, the former must be low given the ease with which water exits through the gallery. As with the drop in the level of the lake as it goes through the process of recovering its equilibrium level, the position of the chemocline also drops, since a flow of water is established from the lake bottom to the underground mine as the system expels mine groundwater, which carries a reduction in the volume of the monimolimnion. In addition to the thickening of the mixolimnion, another consequence observed as a result of the inflow of fresh water is the formation of a new, lower density layer, which stratifies the mixolimnion chemically, resulting in the generation of a new, shallower chemocline that subsequently disappears.

Stage 3 corresponds to a basically dry period with a gradual temperature increase and with the lake at its equilibrium level (Fig. 8C). These conditions trigger thermal stratification of the mixolimnion as its winter chemical stratification weakens until disappearing, resulting in the dispersion of the ephemeral chemocline. Thermal stratification intensifies and causes dissolved oxygen sub-saturation below the thermocline. During this period, the permanent chemocline does not experience any movement and the exchange of water between the lake and the underground mine is null, which inactivates the upwelling of mine groundwater through the old gallery. During this period, the weak ephemeral chemocline moves progressively to greater depths. The erosive descent of this chemocline is due to the maximum relative T that appears in a narrow strip located below it, which destabilizes the water column causing its convective ascent.

Stage 4 corresponds to a dry summer period with high temperatures and high evaporation. The loss of water from the mixolimnion due to evaporation causes the lake level to drop gradually in this period as the thickness of the mixolimnion is progressively reduced. This phenomenon is partially offset by the inflow of mine groundwater from underground mine, which thickens the monimolimnion. As a result, the lake and shafts levels remain below the piezometric level, which favors the supply of groundwater from the rock substrate to the system. The outcome of this overall dynamic is that the chemocline approaches the surface of the lake as its elevation becomes progressively higher (Fig. 8D). During the summer months, the superficial layer increases its EC due to evaporation, which in turn increases the density of the upper layer and facilitates a certain degree of erosion of the chemocline when it begins to cool down after the summer period.

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