



Hydrochemical stratigraphic analysis of the filling of the Meirama mine shaft I: monitoring and filling

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Abstract

The application of an old open-pit lignite mine as an auxiliary reservoir for the supply of the city of La Coruña has involved a detailed analysis of the chemical quality of the vertical profile. The study has shown that a stratified lake is formed where the shape of the filling (first with groundwater and later surface waters from the nearby rivers were added) has influenced the formation of the lake profile. The Meirama mine is an open-pit brown lignite mine located in NW Spain. Exploitation ended in March 2008, leaving a pit of approximately 146 hm³ with a maximum depth of 205 m. The rehabilitation of the pit consisted of the creation of a lake that will serve as an auxiliary water reservoir for the city of La Coruña. The filling process lasted approximately 8 years (March 2008–May 2016) with subterranean and surface contributions from the environment. The formation of an invariant chemocline and a seasonal thermocline was observed. Therefore, in this work, (the first of a series of two articles), an analysis of the evolution of various physicochemical parameters, elements, and compounds at certain heights (the surface, the first 2 m (2 mbs), at 59 masl, and at the bottom (2 masl)). In this first article, the physicochemical parameters of pH, dissolved oxygen, temperature, and some metallic elements (iron and manganese) are analysed. From the analyzed parameters it can be seen the creation of a surface thermocline and a chemocline at a depth of 59 masl with the beginning of the formation of anoxic conditions of the bottom of the pit through the consumption of oxygen.

Keywords Hydrochemical · Open-pit mine · Chemocline · Thermocline

Introduction

The exploitation of the ore of the Meirama mine took place between 1980 and March 2008 (Fig. 1). The generated pit of approximately 146 hm³, 2.2 km in length and 1 km in width was filled with water, initially with groundwater when the operation of the perimeter pumps that kept the mining pit dry during its exploitation was stopped and, since September 2008, by diverting the nearby rivers towards the pit. The obtained lake has a maximum depth of 205 m. This lake will be used as an auxiliary reservoir for supplying the city of La Coruña, located 30 km away, with water since the Abegondo-Cecebre reservoir has become too small to meet the demands of the city (World Bank 2005). This reservoir

is located downstream of the mining lake, which is located at the head of the basin.

The contribution of surface water from September 2009 accelerated the filling since the groundwater contributions, in addition to being of poorer quality, amounted to only approximately 4 hm³/year. Surface inputs improved water quality (Juncosa et al. 2008). There are examples of lake filling in Europe (Schultze et al. 2002, 2011a, b) but not with the exhaustive monitoring done since the origin of the Meirama pit, with more than 800,000 measurements. Thus, monitoring of the hydrochemical quality was carried out during filling (March 2008–May 2016) and postfilling (May 2016–December 2019) to obtain a margin of observation of the different processes that can originate in the lake (Gammons et al. 2009; Zhao et al. 2010).

Initially, vertical samples were taken at three points in the incipient lake (until December 2013). When a depth was reached at which it was found that there was stratification of the lake water regardless of the sampling point, the sampling was reduced to the central point of the lake, as it was the point with the greatest depth. The sampling

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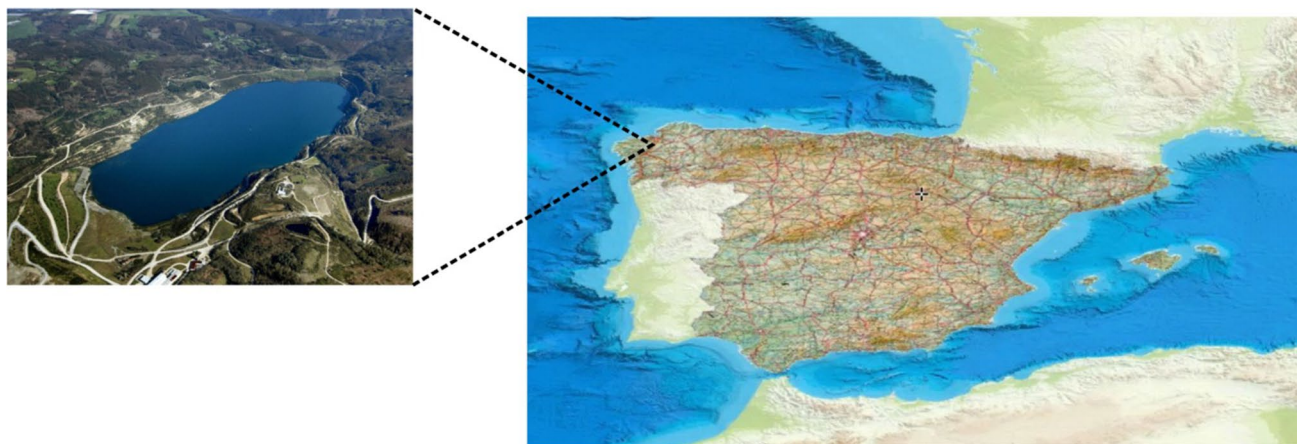


Fig. 1 Location of the Meirama Mining Lake (own elaboration)

occurred monthly, with samples taken every 5 m through the first 40 m of depth and then every 10 m to the bottom. As the water surface increased and taking into account the vertical invariability of the results, the sampling distance was increased to 30 m to the bottom instead of 10 m. Subsequently, starting in January 2013, sampling occurred at every 10 m again.

The parameters and compounds that were selected to obtain as much information as possible within the hydrogeological framework of the environment of the pit to properly understand and interpret the hydrochemistry (Hrdinka 2005; McCullough and Van Etten 2011; Vanderberg et al. 2011) of the filling process were as follows pH, Al, As, Ba, B, Cd, Cr_{total}, Fe_{total}, Fe_{dis}, Mn, Ni, Hg, Pb, Se, Cu, Zn, Ti, Cl, F, SO₄, P_{total}, PO₄, N_{total}, NO₃, NO₂, NH₄, DBO₅, temperature, electrical conductivity, oxidation/reduction potential (ORP), dissolved oxygen, Li, Na, K, Ca, Mg, SiO₂, Br, chemical oxygen demand, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), Ag, Co, Mo, Sb, UO₂, V, and bicarbonate. When the filling was completed in April–May 2016, the elements analysed were reduced to the following: pH, Al, Cd, Fe_{tot}, Fe_{dis}, Mn, Ni, Se, Zn, SO₄, ORP, temperature, electrical conductivity, P_{total}, NO₃, DBO₅, and PO₄.

The physical–chemical parameters of temperature, electrical conductivity, pH, Eh, turbidity and dissolved oxygen were measured in situ every 2 m with a probe throughout the entire filling and postfilling period.

Obtaining a large physical–chemical database has made it possible to carry out some studies and analysis on the rehabilitation of the mining pit as it was being filled. Thus, the application of a predictive model of water quality as the pit was filled has made it possible to introduce corrective techniques to avoid acidification of the lake in its final stage (Delgado et al. 2008, 2014; Juncosa et al. 2018; Fleischammel and Menendez-Lolo 2010; Wolkersdofer 2008). For this

reason, a lime silo was installed in one of the streams leading to the mining hole in order to correct the pH and acidity of the lake. Additionally, it has been possible to validate hydrodynamic models (Hernandez et al. 2012) and solute transport (Delgado et al. 2013) with the data obtained in this filling process.

The quality of the available analytical data was evaluated through the electrostatic balance expected in any natural aqueous solution. This hypothesis, with a physicochemical basis, is generally accepted in hydrochemistry (Appelo and Postma 1992; Hounslow 1995).

Materials and methods

For the execution of the sampling, the conventional techniques described in ISO 5667–1: 2006 (Water Quality 2006), ISO 5667–2: 1991 (Water Quality 1991) and ISO 5667–3: 2003 (Water Quality 2003) were followed. The temperature, electrical conductivity, pH, dissolved oxygen concentration and ORP were measured at the same sampling point of the lake that was being formed. The other parameters were measured in the laboratory according to the methodology defined in APHA (1998) and (Appelo and Postma 1992).

A YSI 556 MPS multiparameter sonde (Yellow Springs Instruments 2006) was used for the measurements in the surface waters. This equipment measures pH (combination glass electrode), ORP (Pt electrode), temperature (YSI PrecisionTM thermistor), electrical conductivity (self-calibrating 4-pole sensor) and dissolved oxygen (“Polarographic steady state” membrane sensor). Additionally, a YSI 6600 V2 sonde was available for the measurement of the vertical profiles in the lake. With this probe, it is possible to measure, in addition to the above parameters, the ORP (Ag/AgCl reference electrode), turbidity (optical mod. YSI 6136 deep turbidity

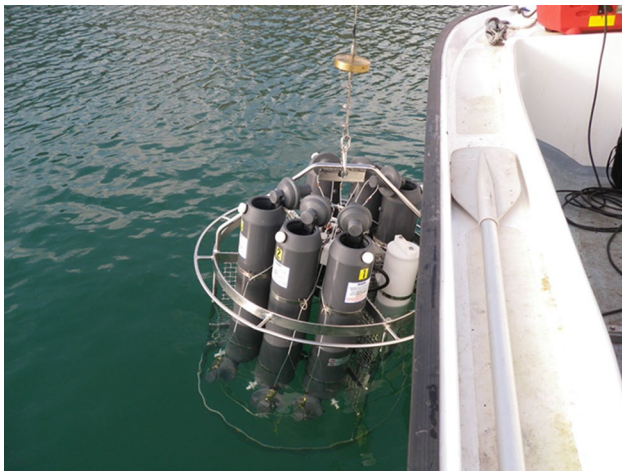


Fig. 2 Carousel sampler

probe) and chlorophyll (optical and self-cleaning mod. YSI 6025 chlorophyll sensor) up to 220 m in depth. The vertical profiles obtained with the measurement of the previous parameters every 2 m were performed with this last probe.

Depth sampling was performed with a Kemmerer-type bottle when the depth reached was not very high. As the pit was filled, the depth increased, so this system was replaced by an automatic system that raised and lowered a carousel-type sampler (SBE 55 ECO water samples) with six bottles with a capacity of 4 L each and a magnetic closure system (Fig. 2). This system allows up to six water samples to be taken at different depths in each dive.

Results and discussion

The following figures show the results obtained for the different physicochemical parameters (temperature, pH, dissolved oxygen, and electrical conductivity) and some cations (Mn and Fe) at different depths: the surface, less than 2 m from the free surface (2 mbs), at 59 m above sea level, and at the bottom (2 masl).

Figure 3 shows the evolution of temperature throughout the period between the beginning of filling and postfilling. A cyclical seasonal variation is observed in the surface according to the time of year (Juncosa et al. 2018) in such a way that a very shallow thermocline is established at a depth of 25 m that is homogenized vertically in the winter seasons. (Miller et al. 1996; Schultze et al. 2011b). In the middle and bottom, parallel behaviour is observed, with very slight variations. However, from the completion of the filling of the pit (April 2016), a decay of 0.0033 °C/day is observed in the bottom and middle zones. Simultaneously, on the surface, the cyclicity is repeated but decreases substantially by approximately 4 °C. It may be that the

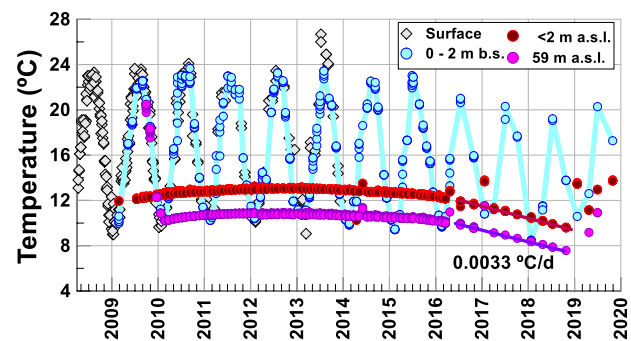


Fig. 3 Temporal evolution of the temperature at the surface, within the first 2 m of depth (2 mbs), at 59 masl, and at the bottom of the pit (2 masl)

external contributions of the streams that discharge into the lake condition the temperature more than the geothermal gradient that comes from the pit. During filling, the water is not renewed, and the source of heat is mainly evaporation. At the time that the discharge begins, the water on the surface is renewed by new contributions, so the thermal flow towards the surface is “accelerated” and the transmission is faster. Note that the pit, once filled, acts as a dam spillway, where the waters from the rivers are those that circulate superficially, thermally renewing the sheet of water.

If we compare the existing temperatures at the bottom (2 masl) and those at 59 masl, it can be seen that there is a second thermocline (very slight), with a higher temperature at the bottom than in the middle area of the lake (Juncosa et al. 2018). This is probably due to the thermal flux from the geological basement, a fact that has been corroborated since January 2019, where the temperature increases at both levels because the geothermal gradient slowly provides constant heat from the geological basement and begins to reach these zones, which results in an increase in temperature. Note that the geological base (granite and schists) has a thermal inertia greater than that of water ($85 \text{ J/m}^2 \cdot \text{K} \cdot \text{s}^{1/2}$ compared to $49 \text{ J/m}^2 \cdot \text{K} \cdot \text{s}^{1/2}$). Thermal inertia is the ability of a material to conserve the thermal energy that it receives and that is released little by little. Therefore, the geological basement is inertially slower, from a thermal point of view, than water, which implies that its effect is perceived in the long term (Lay et al. 2008).

On the other hand, an analysis of the evolution of dissolved oxygen at different depths was carried out, comparing it qualitatively with that presented by different authors in limnological studies carried out in various lakes (Miller et al. 1996; Nürnberg 1995). Thus, the process of oxygen concentration decay was studied, comparing it with the eutrophication behaviour in similar studies (Ramstedt

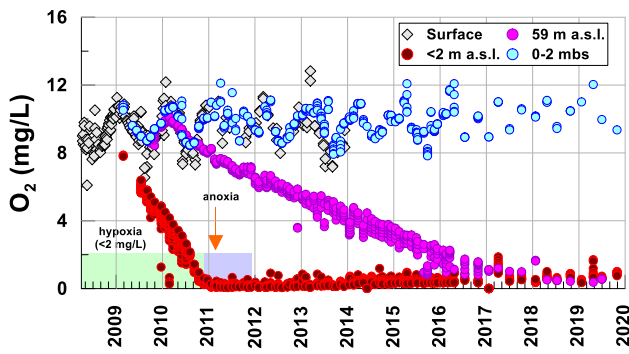


Fig. 4 Temporal evolution of the dissolved oxygen at the surface, within the first 2 m of depth (2 mbs), at 59 masl, and at the bottom of the pit (2 masl)

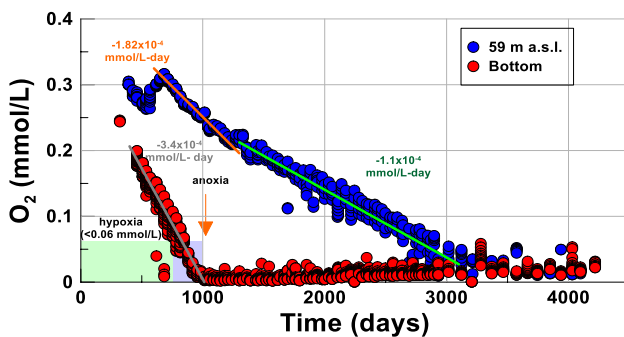


Fig. 5 Decay of dissolved oxygen at 59 masl and at the bottom of the pit (2 masl)

et al. 2003; Carlson 1977; Shevenell et al. 1999) and observing similar behaviour.

The concentration of dissolved oxygen in water is an important indicator of the ecological state of the water (Miller et al. 1996; Nürnberg 1995; Carlson 1977).

The profiles made throughout the filling period (2008–2019) and postfilling period (2016–2019) (starting in winter and ending in summer) show a clear seasonal variation in surface area that attenuates with the depth. The available data clearly show the progressive consumption of oxygen in the deep areas of the lake, with an evident drift towards anoxia (Wetzel 1983; Rzetala and Jagus 2012). This oxygen consumption is due to the oxidation of metals.

Figure 4 shows the temporal evolution in the filling and postfilling periods of the oxygen concentration at the surface of the lake, at 59 masl, and at the bottom of the pit (2 masl). The surface variation is cyclical according to the season of the year, with the water being well oxygenated. However, at 59 masl (a range corresponding to the section considered between 58 and 60 masl), there is a tendency towards oxygen consumption that may be due to the oxidation of metals and organic matter decreasing towards the bottom. The trend

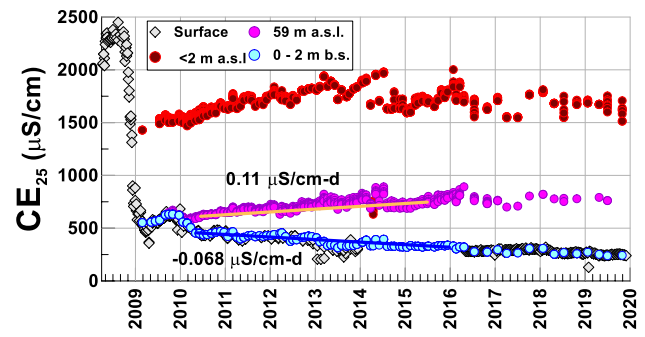


Fig. 6 Temporal evolution of the electrical conductivity at different levels of the lake

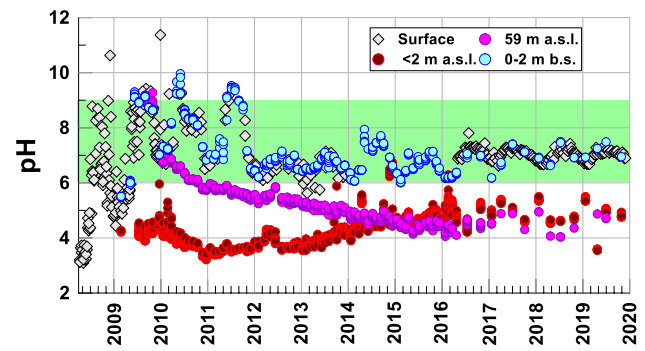


Fig. 7 Temporal evolution of the pH at different levels of the lake

exhibits a depletion rate of $-1.1 \cdot 10^{-4}$ mmol/L-day (Fig. 5), obtaining hypoxic conditions practically at the end of filling.

At the bottom of the pit, the oxygen depletion rate is higher ($-3.4 \cdot 10^{-4}$ mmol/L-day), and the conditions are more anaerobic, reaching anoxic conditions at the end of 2011. This behaviour has been qualitatively observed by various authors, such as Miller et al. (1996), Nürnberg (1995), and Ramstedt et al. (2003).

Figure 6 shows the evolution of the conductivity at different levels. In the surface waters (October 2008), the conductivity at the surface decreases significantly, and as the water level increases, a well-differentiated chemocline is defined in 2010. The conductivity at 59 masl ($0.11 \mu\text{S}/\text{cm}\cdot\text{day}$) and on the surface ($-0.068 \mu\text{S}/\text{cm}\cdot\text{day}$) diverge, which indicates the influence of less ionized waters (Schultze 2012).

At the bottom, variability can be observed, which is determined by precipitation/redissolution processes, with an increase of $0.22 \mu\text{S}/\text{cm}\cdot\text{day}$.

On the surface, the pH (Fig. 7) cycles according to the season of the year, especially after the first years of fluctuations, during which corrective measures were implemented (2008–2012). However, at the bottom and at 59 masl, pH convergence is observed due to the anoxic

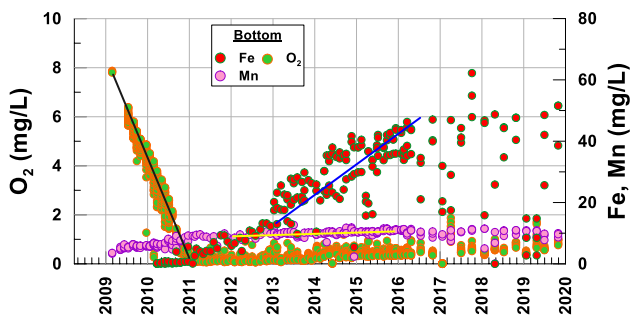


Fig. 8 Decay of dissolved oxygen and temporal evolution of Fe and Mn at the bottom (2 masl)

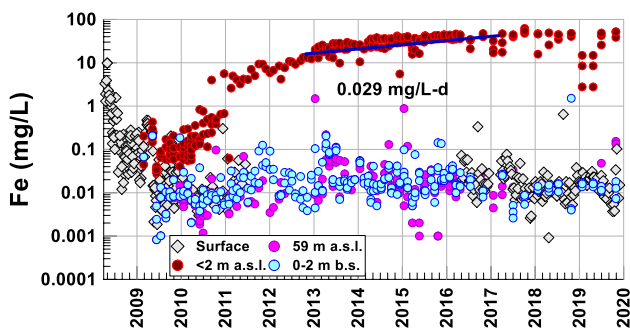


Fig. 9 Temporal evolution of Fe at different levels in the lake

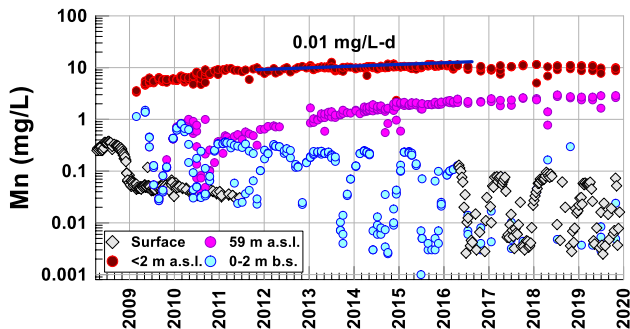


Fig. 10 Temporal evolution of Mn at different levels in the lake

conditions of the lake at this level (Fig. 4), which generate a decrease in pH.

This fact is corroborated in Fig. 8, where the evolution of the dissolved oxygen along with that of Fe and Mn at the bottom of the lake is represented. The redissolution of the precipitated Fe oxides is observed (with an average value of $5.21 \cdot 10^{-4}$ mmol/L-day (0.029 mg/L-day)) at a greater proportion than that of the Mn oxides ($1.81 \cdot 10^{-4}$ mmol./L-day (0.01 mg/L-day)), as these are less soluble, to compensate for the lack of oxygen (Figs. 9 and 10). Oxygen

consumption is related to the decomposition of organic matter, whose contribution comes from higher levels.

Conclusions

The filling of the mining hole has been monitored and it has been possible to verify, in this first article, the evolution of different parameters and elements (T, pH, electrical conductivity, O_{2dis} , Fe, and Mn) in the filling process of the Meirama mining pit was analysed, corroborating the creation of a surface thermocline and a chemocline at a depth of 59 masl with the beginning of the formation of anoxic conditions of the bottom of the pit through the consumption of oxygen. This process led to the initiation of a series of processes of redissolution of metal hydroxides and oxides as a source of oxygen for the decomposition of the organic matter that reaches the mining pit. The second article discusses other sources of oxygen generation from compounds such as nitrate, nitrite, and other metals.

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Author contributions RJ, JD designed the study and led the project. JLC contributed and collected samples.

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Data availability Data will be available upon request.

Declarations

Conflict of interest The authors declare that there are no competing interests.

Ethical standards All authors have read, understood, and have complied as applicable with the statement on “Ethical responsibilities of Authors” as found in the Instructions for Authors and are aware that with minor exceptions, no changes can be made to authorship once the paper is submitted.

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