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Quantifying the potential seepage from porphyry copper tailing impoundments using a multi-isotopic approach



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HIGHLIGHTS

- δ^{2} H- δ^{18} O-H₂O and δ^{34} S- δ^{18} O-SO₄²⁻ allow quantifying the seepage of mine tailing dams.
- Stable isotopes permit to calculate the effectiveness of hydraulic barriers.
- Multi-isotope studies can be implemented for the quantification of groundwater rights.
- This new approach has been fruitfully applied in the Quillayes tailing dam (Chile).

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ABSTRACT

Porphyry-style copper deposits are characterized by low Cu grades and high tonnages, resulting in large mine tailing volumes disposed in impoundments. Due to the mining tailing sizes, waterproofing techniques cannot be applied along the dam base. Therefore, to minimize seepage towards the aquifers, pumping wells are usually installed as hydraulic barriers. Currently, there is a controversy over whether or not the water extracted from hydraulic barriers should be counted as the use of new water rights. Consequently, a growing interest to develop tools to trace and quantify the tailing impacts in groundwater and to determine the water pumped amount subjected to water rights exist. In the present study, isotope data (δ^2 H-H₂O, δ^{18} O-H₂O, δ^{34} S-SO₄²⁻ and δ^{18} O-SO₄²⁻) are proposed as a tool to quantify tailings seepage towards groundwater and to assess hydraulic barriers effectiveness. To illustrate this approach usefulness, the Quillayes porphyry Cu tailing impoundment (Chile) case study is presented. The multi-isotopic approach revealed that tailing waters are highly evaporated showing high SO₄²⁻ content (~1900 mg L⁻¹) derived from primary sulfate ore dissolution, whereas freshwaters, derived from barren host rock. The δ^2 H and δ^{18} O values of groundwater samples collected downstream from the impoundment suggest a mixing at different proportions of highly evaporated water from the mine tailing waters and non-evaporated regional fresh groundwater. Cl⁻/SO₄²⁻, δ^{34} S-SO₄²⁻/ δ^{18} O-SO₄²⁻, δ^{34} S-SO₄²⁻/ δ^{18} O-

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to the impoundment had a mine tailing water contribution from 45 to 90 %, whereas those located farther away had lower contribution (5–25 %). Results confirmed the stable isotope usefulness to determine the water origin and to calculate the hydraulic barrier efficiencies and the pumped water proportions unrelated to the mining tailing subject to the water rights.

1. Introduction

With the acceleration of the global industrialization, world cooper production over the last 110 years has been increasing exponentially (e.g., Singer, 2017). Porphyry deposits are the world's principal source of copper and molybdenum (Cannell, 2004). Porphyry copper deposits consist of disseminated and stockwork sulfide mineralization (Lowell and Guilbert, 1970; Sillitoe, 2010): pyrite, chalcopyrite, bornite, and molybdenite are the major sulfide minerals, although hypogene sulfates, as anhydrite, are generally present.

Chile is worldwide known as host of one of the largest copper concentrations on Earth (Lowell and Guilbert, 1970; Camus and Dilles, 2001; Singer et al., 2008). A total resource of about 455 million tons (Mt) of fine copper has been identified in 54 porphyry copper deposits and numerous prospects (Serrano et al., 1996; Camus and Dilles, 2001; Cannell, 2004). Indeed, the Chilean Andean cordillera contains 9 of the 16 giant porphyries (i.e., deposits with a tonnage > 10 Mt of fine copper) along the circum-Pacific belt (Camus and Dilles, 2001). Currently, Chile annually produces about 5.6 Mt of fine copper that represents about 28 % of the world production (Hammarstrom, 2022). Although Chilean porphyry Cu deposits are characterized by high tonnages (10 to 10,000 Mt), they show low grades of cooper, typically between 0.16 and 1.0 % of Cu (Singer et al., 2008). As a result, large ore volumes are processed requiring large inputs of water, materials, and energy (Aitken et al., 2016; Leiva-González and Onederra, 2022) and generating huge amounts of mine tailings (1,400,000 tons daily, Araya et al., 2020).

The water consumed in copper mining activities is mainly used in the flotation, in the smelting and electro refining, and in the hydrometallurgical processes (Odell, 2021). Water is also used in transport of ore and tailing slurries, dust suppression, equipment washing and human consumption (Kemp et al., 2010). Chile stands out among South American countries as being subject to high levels of water stress. The mining industry accounts for 3.1 % of water consumption (Leiva-González and Onederra, 2022). Based on projections, total water consumption for copper mining in Chile will be $23.3 \text{ m}^3 \text{ s}^{-1}$ by 2031, representing an annual average increment of 2.1 % (Leiva-González and Onederra, 2022). In this context, it should be considered that Chile operates a unique system of private tradable water rights (Chilean Water Code: Budds, 2009; Engler et al., 2021).

More than 99 % of the original material mined from porphyry deposits may be disposed of as waste in mine tailing impoundments that occupy large areas of land (Dold and Fontboté, 2001; Saxena and Dhimole, 2006; Khorasanipour and Eslami, 2014; Khorasanipour, 2015). Indeed, in Chile in 2020, 758 mine tailing impoundments were reported by the cadaster, distributed in 10 of the 16 country regions, 15 % of them active, 62 % inactive, 0.7 % under construction, and 23 % abandoned (Servicio Nacional de Geologia y Mineria, 2022). In consequence, Chile constitutes the third country with more mine tailing impoundments in the world, after China and United States.

Once the ore minerals are recovered by the flotation process, the porphyry cooper tailing slurries contain the remaining fine grained (1–600 μ m) ground-up rock with variable amount of sulfide minerals (typically 1–6 wt% equivalent pyrite, Dold and Fontboté, 2001; Spangenberg et al., 2007), which are mixed with about 50 wt% process waters (Edraki et al., 2014). After entering the mine impoundment, this tailing slurry meanders towards the decantation pond. Water from the decantation pond maybe either discharged through the impoundment into a natural riverbed, or, if possible, recovered and returned to the process (Spangenberg

et al., 2007). Weathering and sulfide oxidation in the impoundments, especially in the unsaturated surface layer, can produce acidic waters with high concentrations of iron, dissolved sulfate (e.g., \sim 25,000 mg L⁻¹; Dold and Spangenberg, 2005) and potentially hazardous trace metal elements (e.g., Khorasanipour et al., 2011; Lottermoser, 2012; Khorasanipour and Eslami, 2014).

Due to the large size of the mining tailings, which does not allow the application of waterproofing techniques along their entire length, there is a high risk of seepage of polluted water from the Tailing Storage Facility (TSF) towards downstream groundwater (e.g., Sharma and Al-Busaidi, 2001; Lottermoser, 2012; Mohapatra and Kirpalani, 2017). Drainage ditches, cut-off walls or pumping wells installed downstream as hydraulic barriers are usually used to minimize polluted seepage towards groundwater and to protect and remediate groundwater (Millano et al., 1993; Anderson and Mesa, 2006; Duda, 2014). The pumping wells installed as hydraulic barriers collect both mine tailing seepage waters and fresh groundwater. Regarding Chilean water allocation, mine tailing water should not consume water rights because it has been previously used on the mining operations, whereas fresh groundwater consumes water rights contracted by the mining company. Hence, a current interest exists to develop and implement tools to quantify the contribution of both water types in the total water mass pumped from the hydraulic barrier wells and to trace and quantify the impact of mine tailings in neighboring groundwater.

Several isotope studies have been carried out to trace water sources and pathways and to gain insight about the oxidation processes in mine tailing impoundments from porphyry copper deposits (Ghomshei and Allen, 2000; Hazen et al., 2002; Seal, 2003; Dold and Spangenberg, 2005; Smuda et al., 2006; Spangenberg et al., 2007). Sulfur and oxygen isotopic composition of dissolved sulfate (δ^{34} S-SO₄²⁻ and δ^{18} O-SO₄²⁻), which is a powerful tool to trace the origin of sulfate in environmental studies (Clark and Fritz, 1997), has been applied to trace Cu-Mo porphyry mine tailings impact (e.g., Dold and Spangenberg, 2005). The δ^{34} S-SO₄²⁻ and δ^{18} O-SO₄²⁻ ranges of the main sulfate sources (i.e., sulfate minerals dissolution, fertilizers, and sulfide oxidation) are usually defined according to the extreme values reported in the literature (e.g., Newman et al., 1991; Krouse and Mayer, 2000; Dogramaci et al., 2001; Vitòria et al., 2004). Sulfate derived from dissolution of evaporites (e.g., gypsum, anhydrite) generally has high δ^{34} S-SO₄²⁻ values (+10 to +30 ‰: Li et al., 2014), while sulfate from sulfide oxidation often shows negative δ^{34} S-SO₄²⁻ values (Balci et al., 2007, 2012). In contrast to sulfate originating form anhydrite dissolution, sulfate derived from sulfide oxidation does not show the δ^{18} O of the original mineral, but δ^{18} O values resulting from the equilibrium with water and atmospheric O2 (Krouse and Mayer, 2000; Kohl and Bao, 2011) depending on the oxidation pathway. For example, since pyrite oxidation usually involves atmospheric O2 and H2O (Eq. (1)) or ferric iron (Eqs. (2) and (3)) (Lipfert et al., 2007), oxygen in sulfate derived from pyrite (or sulfides) oxidation comes from either atmospheric oxygen $(\delta^{18}\text{O-O}_2 = +23.5 \text{ }$ %: Kroopnick and Craig, 1972), or from meteoric water (δ^{18} O-H₂O).

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
 (1)

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O$$
 (2)

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$
 (3)

Experimental studies developed by Van Stempvoort and Krouse (1994) concluded that the minimum $\delta^{18}O$ -SO₄²⁻ value derived from sulfide

oxidation is the value of local water (δ^{18} O-H₂O), whereas the maximum δ^{18} O can be calculated using Eq. (4):

$$\delta^{18} O(SO_4^{2-}) = 0.62 \cdot \delta^{18} O(H_2 O) + 9 \tag{4}$$

Therefore, the δ^{18} O of dissolved sulfate provides an additional tracer. Furthermore, both δ^{34} S-SO₄²⁻ and δ^{18} O-SO₄²⁻ values may be affected by processes producing isotopic fractionation, such as bacterial sulfate reduction or bacterial disproportionation of sulfur intermediates (Canfield, 2001; Guo et al., 2016).

Despite several studies applied isotopic tools to porphyry copper mine tailing impoundments, they mainly focused on tracing water sources and pathways, whereas only a few studies used these tools for quantifying tailings seepage towards aquifers (e.g., Allen and Voormeij, 2002). Based on our knowledge, the isotope geochemistry has never been applied so far to quantify the effectiveness of hydraulic barriers installed in mine tailing impoundments and the fraction of pumped water that is subject to water rights. Therefore, the aim of this study is to demonstrate the usefulness of isotope tools (δ^{34} S-SO²₄⁻ and δ^{18} O-SO²₄⁻ and δ^{2} H-H₂O and δ^{18} O-H₂O) to quantify: i) the mine tailing waters contribution to groundwater; ii) the effectiveness of hydraulic barriers to mitigate tailing impoundments seepage to groundwater; and iii) the water rights that the mining companies consume in the extraction of water from pumping wells installed as hydraulic barriers. This new approach is illustrated in the Quillayes porphyry Cu tailing impoundment (Chile).

2. Materials and methods

2.1. Site description and sample collection

The TSF investigated corresponds to the Quillayes impoundment of "Los Pelambres" porphyry copper deposit, which is owned and operated by Antofagasta Minerals. The impoundment is located in the Chacay Stream area (Coquimbo Province, Chile) at an average altitude of 1400 m above sea level (masl). It was constructed on the Cuncumén River valley, a tributary of the Choapa River, approximately 4 km downstream from the confluence of the Piuquenes, Pelambres, and Chacay Streams (Fig. 1). The Quillayes TSF stored the mine tailings generated from 1988 to 2008 (close to 78,000,000 m³), until the dam's maximum (198 m height) was reached. The currently active TSF of the Los Pelambres mine is the Mauro impoundment. Geologically, the Quillayes impoundment foundation consists of fluvial deposits in the central area, colluvial and alluvial terraced deposits in the left margin and granodiorites in the right margin.

Several surface and groundwater management strategies are used for intercepting and diverting surface water runoff reaching the TSF area and for avoiding seepage from the TSF to the downstream aquifer (Campaña et al., 2015). The most important points are briefly described as follows. The Quillayes mine tailing impoundment is delimited by two dams: i) an embankment dam located upstream, referred to as Tail Dam, with a maximum height of 40 m and a crest wide of 8 m, which was constructed to store surface freshwaters and prevent their interaction with mine tailing



Fig. 1. General layout and cross-section of the Quillayes porphyry copper tailing impoundment showing surface and groundwater management strategies and sample locations for the current study.

waters; and ii) the Frontal Dam, an embankment dam that retains the mine tailings. A Diversional Tunnel of 5.45 m width and 6.0 km length, designed to convey a flow of slightly >400 m³ s⁻¹, was constructed to divert surface water from the Tail Dam and return it to its natural course at a gully located downstream from the toe of the Frontal Dam (Campaña et al., 2015) (Fig. 1). A 7 to 15 m-deep cut-off trench was excavated at the base of the Frontal Dam to intercept seepage waters (Campaña et al., 2015), which are stored through a Toe Dike. Downstream of the TSF, 8 wells were installed forming two hydraulic barriers to pump the potential seepage waters from the TSF and to monitor groundwater quality. The 1st hydraulic barrier, located near the TSF, is constituted by AB-6C, ABQ-6 ABQ-9, and ABQ-9A pumping wells, whereas ABQ-6-7A, ABQ-7, ABQ-7D and ABQ-8A pumping wells conform the 2nd hydraulic barrier, located downstream (Fig. 1). The pumped groundwater is returned to the interception seepage trench.

Due to water scarcity in the region, a water recovery system from the dam area was installed to recover surplus water from the tailing disposition and from seepage occurring through the dam and its foundations (Campaña et al., 2015). With this system, the process water used in the mine flotation consists of approximately 85 % of recycled water, whereas the remaining 15 % comes from surrounding local surface water and groundwater sourced at 1600 masl. For example, in 2013, the mine used 4462 L s⁻¹ of water, with recycling water accounting for 85.14 % of the total. Therefore, only 14.86 % (663 L s⁻¹) can be considered as water consumption, which constitutes 49.48 % of the total water right (1340 L s⁻¹) available for mining operations.

Climatologically, the study area is characterized by a dry season from November through April and a rainy season that occurs during May to August. In order to identify possible seasonal changes during the rainy and dry seasons, two samplings at Quillayes TSF and surrounding surficial and groundwater were performed: one in November 2016 (dry season) and other in August 2017 (end of rainy season). A total of 57 water samples (28 in November 2016 and 29 in August 2017) were collected for chemical and stable isotope analyses. The sampling locations are shown in Fig. 1 and geographical and hydrogeology information for each surface and groundwater sampling point is summarized in Table SI-1. Surface water was collected in the Piuquenes, Pelambres, Chacay and Cerro Blanco streams, which are located upstream of the Quillayes TSF, as well as along the Cuncumén and Choapa Rivers, which are ubicated downstream of the mine tailing impoundment. Three additional surface water samples were taken: freshwaters from the Tail Dam, seepage waters stored at the base of the Toe Dike, and water from the Diversional Tunnel discharge. Water samples from the saturated zone (>2 m depth) were obtained from installed piezometers (P-13C and P-06). Groundwater samples were collected from piezometers, monitoring wells, and pumping wells installed as hydraulic barriers. All these samples can be grouped in five zones (Fig. 1): i) samples upstream of the TSF (Zone 1); ii) unsaturated and saturated zone of the Quillayes mine TSF (Zone 2); iii) samples downstream of the TSF in the area of the 1st hydraulic barrier (Zone 3); iv) samples situated farther from the TSF in the area of the 2nd hydraulic barrier (Zone 4); and vi) samples in the agricultural area of Cuncumén and Choapa Basin (Zone 5).

Two tailing samples from the unsaturated zone of the Quillayes TSF were obtained, one from the TSF decantation pond (REL 2017) and one from the TSF lateral margin where the tailings slurry meanders forming a relatively dry area (REL 2016). These samples, constituted by fine grained ground-up rocks mixed with water, were collected to analyze the water and dissolved sulfate isotopic composition, and to characterize the isotopic composition of sulfide and sulfate minerals of the solid fraction. Additionally, a sample constituted only by water was also obtained from the decantation pond (CLAS AS 1). Finally, a sample of the ore pulp produced in the flotation plant was collected to analyze the sulfur isotopic composition of ore sulfides.

2.2. Chemical and isotopic analysis

Surface and groundwater pH and electrical conductivity parameters were measured in situ using portable electrodes. The measurements were directly taken from the water flow of streams, whereas groundwater measurements were conducted using a flow-through chamber to minimize the effect of air exchange. All the wells were purged prior to sampling by either removing a minimum of three well volumes or until the electrical conductivity was stabilized. Surface water samples were obtained using an extendable pole (2 m long) with a HDPE bottle at one end. Before taking the samples, the bottle was rinsed 3 times with surface water at the sampling point. All water samples were filtered with a Millipore® filter (regenerated cellulose) of 0.45 μ m pore size and stored in the dark at +4 °C in air-sealed standard polyethylene bottles (PET) prior to chemical and isotope analysis following official standard methods (APHA, 1998). Chemical parameters weredeterminedviætandardanalyticaltechniquesmajoranions(Cl⁻,

 SO_4^{2-} and NO_3^-) were determined by High-Performance Liquid Chromatography (HPLC), and major cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) were measured by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) using an Optima 2100 DV (Perkin Elmer) after samples acidification to pH <2 using ultrapure nitric acid (HNO₃). The chemical analyses were performed in the *Laboratorio de Isótopos Ambientales* of the *Comisión Chilena de Energía Nuclear* (CCHEN).

The water-soluble sulfate minerals of the two solid mine tailing samples were obtained by mixing a 5 g of dried, homogenized and quartered solid tailing aliquot with 300 mL of deionized water during 4 h under agitation at 50 °C. Once the sulfate was leached, the remaining tailing was filtered with a Millipore® filter of 0.45 μ m and sulfides were concentrated by manual panning. Sulfate from the 58 water samples and the leachates from the 2 tailings was precipitated as BaSO₄ by adding BaCl₂·2H₂O after acidifying the sample with HCl and boiling it to prevent BaCO₃ precipitation, following standard methods (Dogramaci et al., 2001). The BaSO₄ was separated from the solution by filtering through a 0.45 μ m NH₄-acetate filter.

Stable isotopes are usually measured as the ratio between the rare isotope and the abundant isotope (e.g., ³⁴S against ³²S). The isotope compositions of sulfur, oxygen and hydrogen are reported in delta (δ) notation as the per mil (‰) deviations of the isotope ratio relative to known international reference standards (Eq. (5)):

$$\delta_{\text{sample}} = \left(R_{\text{sample}} / R_{\text{standard}} \right) - 1 \tag{5}$$

where $R = {}^{34}\text{S}/{}^{32}\text{S}$, ${}^{18}\text{O}/{}^{16}\text{O}$ and ${}^{2}\text{H}/{}^{1}\text{H}$ in the sample and the standard, and is expressed as ‰ (Coplen, 2011). The following isotopic compositions were determined in this study: i) sulfur isotopic composition of sulfides from the mine tailings and pulp ($\delta^{34}\text{S}_{\text{sulfides}}$); ii) sulfur and oxygen isotopic composition of sulfate dissolved in water and water-soluble sulfate minerals from mine tailings ($\delta^{34}\text{S}-\text{SO}_4^{2-}$ and $\delta^{18}\text{O}-\text{SO}_4^{2-}$); and iii) deuterium and oxygen isotopic composition of water ($\delta^{2}\text{H}-\text{H}_2\text{O}$ and $\delta^{18}\text{O}-\text{H}_2\text{O}$). Notations are expressed as δ relative to the international reference standards: V-CDT (Vienna Canyon Diablo Troilite) for sulfur, and V-SMOW (Vienna Standard Mean Oceanic Water) for hydrogen and oxygen.

The δ^{34} S analyses of sulfides and sulfates were conducted with a Carlo Erba EA-Finnigan Delta C Isotope Ratio Mass Spectrometer (IRMS), whereas the δ^{18} O of sulfates was analyzed with a ThermoQuest high temperature Conversion Elemental Analyzer (TC/EA) coupled in continuous flow with a Finnigan MAT Delta C IRMS. The δ^{2} H-H₂O and δ^{18} O-H₂O values were determined by Wavelength Scanned Cavity Ringdown Spectroscopy (WS-CRDS; L2120-i Picarro®, Picarro Inc., Sunnyvale, CA, USA). According to Coplen (2011), raw isotope values were normalized using several international and laboratory standards. The international and laboratory standards used, as well as the reproducibility of the samples, are shown in SI-2. The δ^{2} H-H₂O and δ^{18} O-H₂O analyses were determined in the *Centro de Hidrogeología* of the *Universidad de Málaga* (CEHIUMA). All the other isotopic values were determined at the *Centres Científics i Tecnològics* of the *Universitat de Barcelona* (CCIT-UB).

3. Results and discussion

Chemical and isotopic results of the Quillayes mine tailing waters and surrounding groundwater and surface waters obtained in the sampling

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survey of November 2016 and August 2017 are shown in Tables SI-3a and SI-3b, respectively.

3.1. Source apportionment and mine tailing quantification using chemical data

In contraposition to freshwaters located upstream from the Quillayes TSF (i.e., pre-impoundment surface water and groundwater), mine tailing waters in saturated (P-13C) and unsaturated (CLAS AS 1) zones are characterized by high conductivity and high dissolved sulfate (~2000 mg L⁻¹), calcium (~700 mg L⁻¹), and chloride (~300 mg L⁻¹) concentration. Groundwater samples located downstream of the TSF showed conductivity, SO_4^{2-} , Ca^{2+} and Cl^- values comprised between mine tailing waters and freshwaters, suggesting a mixing at different proportions of both water types. In order to evaluate the contribution of mine tailing waters to surface and groundwater, a simple mixing model between mine tailing waters and freshwater was applied using Cl^- and SO_4^{2-} concentrations. Following Faure (1986), a two-component mixing model can be described with Eqs. (6) and (7).

$$f = \frac{A}{A+B} \tag{6}$$

$$X_{\rm M} = X_{\rm A}f + X_{\rm B}(1-f) \tag{7}$$

where f is the weight fraction of A in the A + B mixture, X_M is the concentration of element X in the mixture, and X_A and X_B are the concentration of element X in components A and B, respectively. The freshwater endmember considered was sample MC-Q from the "Tail Dam". Although water stored in this Dam can be affected by evaporation, it represents an average composition of surficial freshwater, since it collects surface waters of Pelambres River and its tributaries. The sample CLAS AS 1 was considered as the mining end-member. A second mixing model was also calculated between mining end-member (CLAS AS 1) and sample P-23, considered as representative of lateral freshwater inflow (Fig. 2).

Samples collected in Zone 2 (impoundment area) either show mining values (P-13C) or lie in the mixing line between freshwater and mining water (Dren and P-06). The two latter can be either explained by a mixing between lateral inflow freshwaters and mine tailing waters (with lateral inflow contributions of 20 and 44 % in Dren and P-06, respectively) or by a

mixing between regional freshwater and mine tailing waters (with similar percentages of freshwater contribution) (Fig. 2). Thus, the Cl^- vs. SO_4^{2-} mixing model led to uncertainty in the freshwater type contribution involved in Dren and P-06 samples: regional recharge or lateral inflow. The observed differences in mine tailing contribution in Zone 2 area suggest that the saturated zone of the Quillayes TSF is heterogeneously affected by groundwater circulation, as occurs in other Chilean porphyry cooper tailing impoundments: Cáren and Cauquenes from "El Teniente", Piquenes from "La Andina" and Talabre from "Chuquicamata" ore deposits (Spangenberg et al., 2007).

Samples collected in Zone 3 (1st hydraulic barrier, SO_4^{2-} : 1000–1500 mg L⁻¹), show a mine tailing contribution ranging from 50 to near 80 %, except samples from well ABQ-6, with no contribution from mine tailing water. Samples collected in Zone 4 (2nd hydraulic barrier; SO_4^{2-} : 200–700 mg L⁻¹) had a mine tailing water proportion lower than ~30 % (Fig. 2).

3.2. Source and end-member characterization using $^{34}\mathrm{S}$ and $^{18}\mathrm{O}$ of dissolved sulfate

Porphyry copper deposit of "Los Pelambres" is characterized by a hydrothermal potassic alteration, constituted by potassium feldspar with anhydrite, biotite and chalcopyrite, and to a lesser extent bornite, digenite and molybdenite (Sillitoe, 1973). Consequently, the presence of sulfate minerals (mainly anhydrite) and residual non-recovered barren or non-economic ore sulfides (pyrite, chalcopyrite, bornite, digenite, molybdenite) in the Quillayes TSF is expected. Therefore, three potential SO_4^{2-} sources have been considered: i) dissolution of hypogene ore sulfates of "Los Pelambres" deposit (e.g., pyrite, chalcopyrite); and iii) agrochemical fertilizers. Fig. 3 shows the $\delta^{34}S-SO_4^{2-}$ and $\delta^{18}O-SO_4^{2-}$ of these potential sources together with the three end-members observed in the chemical mixing models: regional freshwater, mine tailing water and lateral inflow waters.

Although there are no reported isotopic values of sulfides and hypogene sulfate of the "Los Pelambres" ore deposit, it is predictable that they will show values similar to those reported from close porphyry copper deposits, e.g. the "El Teniente" ore, which shows: i) δ^{34} S values of sulfides (chalcopyrite, pyrite, molybdenite and bornite) ranging from -5.9 to +2.4 ‰



Fig. 2. Cl^{-} vs. SO_4^{2-} diagram showing mixing models between mine tailing water (CLAS AS 1) and freshwater (upstream freshwater, MC-Q, and lateral inflow waters, P-23) end-members. Samples from both sampling surveys are represented. Green and pink boxes correspond to regional freshwater and mine tailing water end-members, respectively. GW: groundwater; SW: surface water.



Fig. 3. Plot of δ^{34} S versus δ^{18} O for SO₄²⁻ in the Quillayes tailing impoundment waters and surrounding freshwaters. Isotopic data of primary ore sulfates (anhydrite) are from Kusakabe et al. (1984) and Cannell (2004), fertilizers from Vitòria et al. (2004) and isotope values of sulfate from sulfide oxidation were calculated according to Van Stempvoort and Krouse (1994) and using δ^{34} S values of ore sulfides from Cannell (2004). Mixing models (expressed as % of dissolved sulfate) between sulfate dissolution and sulfide oxidation are also depicted. The same colors that in Fig. 2 are used for representing regional freshwater (green box) and mine tailing water (pink box) end-members. Note that dissolved sulfate from seepage of the impoundment (DREN) and mine tailing water in saturated zone (P-06) plot in the mixing line between SO₄²⁻ of mine tailing water from unsaturated zone and lateral inflow freshwater. GW: groundwater; SW: surface water.

(Cannell, 2004); and ii) δ^{34} S-SO₄²⁻ and δ^{18} O-SO₄²⁻ of anhydrite comprised between + 8.6 and + 15.5 ‰ and from + 6.8 to + 10.6 ‰, respectively (Kusakabe et al., 1984; Cannell, 2004; Fig. 3). The measured isotopic composition of sulfides (δ^{34} S = -1.8 to +4.4 ‰) and water-soluble sulfate minerals (δ^{34} S-SO₄²⁻ = +9.6 to +9.8 ‰; δ^{18} O-SO₄²⁻ = +6.1 to +8.6 ‰) in the tailing solid fraction of the TSF unsaturated zone and in the ore pulp (see SI-3) is consistent with the theoretical isotopic compositions at ore deposit scale.

Appling Eq. (4) and using the maximum δ^{18} O-H₂O value obtained in this study (-9.6 ‰, sample CLAS AS1) we estimated the theoretical δ^{18} O range of dissolved sulfate derived from sulfide oxidation at ore deposit scale (δ^{18} O = -9.6 to +3.0 ‰). The same calculation but using δ^{18} O-H₂O values obtained in mine tailing water (-11.1 to -10.0 ‰, samples REL-2016 and REL-2017) and the average δ^{18} O-H₂O composition of freshwaters located upstream of the Quillayes TSF (-13.2 ‰) was used to estimate the δ^{18} O range of dissolved sulfate derived from sulfide oxidation at TSF scale (δ^{18} O = -1.1 to +2.8 ‰). Values are also consistent with the theoretical isotopic compositions at ore deposit scale (Fig. 3).

Sulfate isotopic characterization of different synthetic fertilizers, collected from different commercial suppliers, was reported by Vitòria et al. (2004), showing a sulfur and oxygen isotopic range of -0.7 to +10.7 ‰ and +9.2 to +14.8 ‰, respectively (Fig. 3).

Isotopic mixing models between SO_4^{2-} derived from sulfide oxidation and sulfate dissolution were calculated using Eqs. (6) and (7). Results are shown in Fig. 3. Sulfates in regional freshwaters samples, located upstream of the TSF, are derived from sulfide oxidation, except for samples from site 8 AS. This is consistent with the fact that regional freshwaters drain the "Los Pelambres" porphyry copper deposit and interact with sulfide enriched rocks. Samples from site 8 AS show SO_4^{2-} contributions from sulfide oxidation (55 to 60 %), but also from sulfate mineral dissolution. Mine tailing waters in unsaturated zone of the TSF (REL-2016, REL-2017 and CLAS AS 1) show 20 to 35 % contribution of SO_4^{2-} derived from sulfide oxidation, whereas samples from the underlaying saturated zone (P-13C) show a 95 % influence of sulfate mineral dissolution with a minimum contribution from sulfide oxidation, which can be linked with the low dissolved oxygen at these depths ($<10 \text{ mg L}^{-1}$, Spangenberg et al., 2007). Thus, the unsaturated surface layer shows higher contribution of sulfate derived from sulfide oxidation than the saturated zone, as occurs in other Chilean porphyry copper TSF (Dold and Spangenberg, 2005).

Finally, it is noteworthy that isotopic values of sulfate in lateral inflow freshwater (P-23) do not fit with any potential geogenic sources. One feasible explanation is the contribution of sulfates derived from sulfide oxidation that have undergone bacterial reduction processes. An additional mixing model between mine tailing waters and lateral inflow waters was thus applied (Fig. 3). Seepage waters collected in "Toe Dike" (DREN) and mine tailing waters in the saturated zone (P-06) show a SO_4^{2-} contribution from lateral inflow freshwater of 20 and 40 %, respectively, in agreement with the contribution suggested using the Cl⁻ and SO_4^{2-} model (Fig. 2).

3.3. Source and end-member characterization using ²H and ¹⁸O of water

Fig. 4 shows the δ^2 H-H₂O and δ^{18} O-H₂O of the three end-members used in the chemical and δ^{34} S-SO₄²⁻ vs. δ^{18} O-SO₄²⁻ mixing models: regional freshwater, mine tailing water and lateral inflow waters. Regional freshwaters from Zone 1 show δ^2 H-H₂O and δ^{18} O-H₂O values that vary along the calculated Local Meteoric Water Line (LMWL, see SI-4 for its calculation). The observed dispersion can reflect a seasonal variability and/or an altitudinal gradient effect of rainfall recharge, both related to atmospheric temperature changes (e.g., Clark and Fritz, 1997; Kendall and Doctor, 2003). δ^{2} H-H₂O and δ^{18} O-H₂O variability along the LMWL can also reflect mixing processes between water with different isotopic signature according to their different altitudinal origin. For example, surface water from the Pelambres River (18 AS), shows lower δ^2 H-H₂O and δ^{18} O-H₂O values than its tributary the Chacay Stream (8 AS), linked to an isotopic gradient with the recharge altitude, being lower in the Chacay Basin (~2500 masl) than in Pelambres Basin (~2700 masl). Sample 1 AS, located in Pelambres River downstream of the Chacay Stream confluence, shows δ^2 H-H₂O and δ^{18} O-H₂O values that can be explained by a mixing between 18AS and 8 AS. The observed difference between 1 AS in both field surveys suggests a seasonal effect: with a lower contribution from Chacay stream in November



Fig. 4. Plot of δ^2 H versus δ^{18} O for freshwaters (regional surface and groundwater, and lateral inflow water) and mine tailing and seepage waters from the Quillayes tailing impoundment. Local Meteoric Water Line (LMWL) after IAEA/WMO (2021): δ^2 H = 7.8· δ^{18} O + 6.5. Mixing models (expressed as % of water) between freshwater and evaporated mine tailing water, as well as from 18AS and 8AS samples are also depicted. The same colors that in Figs. 2 and 3 are used for representing regional freshwater (green box) and mine tailing water (pink box) end-members. See Supporting information SI-4 for Local Evaporation Line (LEL, δ^2 H = 5.2· δ^{18} O - 28.0) and water evaporation rates determination. GW: groundwater; SW: surface water.

2016. In any case, chemical and δ^2 H-H₂O and δ^{18} O-H₂O data suggest that surface and groundwater in Zone 1 originates from rainfall recharge at different altitudes.

Samples collected in Zone 2 from the "Tail Dam" (MC-Q), and from the TSF unsaturated (CLAS AS1, REL-2016 and REL-2017) and saturated (P-13C) zones, show δ^2 H-H₂O and δ^{18} O-H₂O values that depart from the LMWL following a linear trajectory, in agreement with an evaporation trend (Fig. 4). Evaporation causes an increase in δ^2 H-H₂O and δ^{18} O-H₂O values in the residual water, producing a positive linear trend departing from the precursor water, with a slope between 4 and 6 (Clark and Fritz, 1997; Gonfiantini, 1986). This linear trajectory, called Local Evaporation Line (LEL), was calculated according to equations presented in Supporting information SI-4, resulting in the equation: δ^2 H = 5.2 $\cdot\delta^{18}$ O – 28.0. The LEL agrees with the warm-summer Mediterranean climate of the study area, and no positive displacement of the δ^2 H-H₂O values due to H-isotope exchange with H-bearing volatile phases occurs, as it was observed in other Chilean mine TSF (Spangenberg et al., 2007).

Samples from the lateral inflow (P-23) show δ^2 H-H₂O and δ^{18} O-H₂O values similar to regional waters. Therefore, using δ^2 H-H₂O and δ^{18} O-H₂O data, these two endmembers cannot be distinguished and the mixing model between mine tailings and regional freshwater or lateral inflow overlaps the LEL.

Maximum evaporation is observed in samples from the TSF unsaturated zone (CLAS AS 1, REL 2017; ~25 %), although seasonal variability is observed in sample REL 2016, located on the lateral margin, and less affected by evaporation (15 %). For this sample, a contribution of freshwater from regional recharge or lateral inflow cannot be ruled out. Samples from the TSF saturated zone (P-13C and P-06) are also less evaporated (~18 % and ~12 % respectively). Cl⁻ vs. SO₄²⁻ (Fig. 2) and δ^{34} S-SO₄²⁻ vs. δ^{18} O-SO₄²⁻ (Fig. 3) mixing models indicate that there is no freshwater contribution in sample PC-13C, but some for sample P-06. Applying the δ^{2} H-H₂O vs. δ^{18} O-H₂O model, a mixing of lateral inflow freshwater and mine tailing waters with a 70 % and 30 % proportion, respectively, is obtained. The fraction of

evaporated water in the "Tail Dam" (~8 %, MC-Q) is lower, which is consistent with its lower residence time, since it is diverted through the tunnel. δ^2 H-H₂O and δ^{18} O-H₂O values of seepage waters collected in the Toe Dike (DREN) can also be explained either by evaporation (20 %) or by mixing between lateral inflow freshwater and mine tailing waters (20–25 % of freshwater). Therefore, using δ^2 H-H₂O and δ^{18} O-H₂O data there is higher uncertainty in the determination of the contribution of the different end-members.

3.4. Source apportionment using multi-isotopic data downstream of the TSF

Three different mixing models were applied to determine the contribution of the different end-members to groundwater collected downstream of the TSF.

First, a δ^2 H-H₂O vs. δ^{18} O-H₂O mixing model between highly evaporated mine tailing waters (REL and CLAS AS 1 samples) and non-evaporated regional freshwaters was applied (Fig. 5). Using this model, a high mine tailing water contribution is estimated in both groundwater (from 40 to 90 %, except ABQ-6) and surface water (C3, 50-60 %) samples from Zone 3. Groundwater samples from Zone 4 show a lower tailing water proportion (< 25 %). All these proportions are consistent with the results obtained using the Cl^{-}/SO_{4}^{2-} ratio (Fig. 2). Samples ABQ-6 and 1 AM-8 do not show contribution of mine tailing water, suggesting that they are sourced from surface freshwater discharged through the Diversional Tunnel. which is also in agreement with the chemical data model. The δ^2 H-H₂O vs. δ^{18} O-H₂O model, therefore, allows the determination of mine tailing influence in Zone 3, located close to the TSF, but there is a high uncertainty to determine mine tailing contribution in samples from Zone 4 as the isotopic composition overlaps with that for regional freshwaters. Nevertheless, mine tailing contribution in these samples would be <25 %, approximately.

Second, a δ^{34} S-SO²₄ vs. δ^{18} O-SO²₄ mixing model between dissolved sulfate from mine tailing waters and from regional freshwaters was applied (Fig. 6). Using this model, samples from Zone 3, except ABQ-6, show a sulfate contribution from mine tailing waters higher than 85 %, whereas



Fig. 5. Mixing model between δ^2 H and δ^{18} O, showing freshwater (green box) and mine tailing water (pink box) end-members. Samples of groundwater collected downstream to the Quillayes tailing impoundment plot in the mixing area (orange box: 1st hydraulic barrier wells, corresponding to Zone 3; yellow box: 2^{on} hydraulic barrier, Zone 4), whereas groundwater and surface waters obtained in crops along Cuncumén and Choapa rivers plot near the Local Meteoric Water Line (LMWL). GW: groundwater; SW: surface water.



Fig. 6. Mixing model between δ^{34} S and δ^{18} O-SO₄²⁻, showing SO₄²⁻ from freshwater (green box) and mine tailing water (pink box) end-members. Samples of groundwater collected downstream to the Quillayes tailing impoundment show δ^{34} S-SO₄²⁻ and δ^{18} O-SO₄²⁻ that plot in the mixing area (orange box: 1st hydraulic barrier, Zone 3; yellow box: 2^{on} hydraulic barrier, Zone 4), whereas groundwater and surface waters obtained in crops along Cuncumén and Choapa rivers (Zone 5) show SO₄²⁻ compositions that plot gradually to fertilizers (Vitòria et al., 2004). GW: groundwater; SW: surface water.

samples from Zone 4 have a tailing contribution ranged from 25 to 65 %. These percentages are higher than the ones obtained using chemical data (Fig. 2) and water isotopes (Fig. 5), because this simple mixing model (Eqs. (6), (7)) does not include water mass proportions as occurs with Cl⁻ vs SO₄²⁻ and δ^2 H-H₂O vs. δ^{18} O-H₂O mixing models. Nevertheless, this limitation is improved with the δ^{34} S-SO₄²⁻ vs. Ln(SO₄²⁻) presented in Fig. 7.

Thirdly, a more detailed mixing model developed by Faure (1986) was applied (Eq. (8)):

$$\delta^{34}S_{M} = \frac{\left[SO_{4}^{2}^{-}\right]_{A}\left[SO_{4}^{2}^{-}\right]_{B}\left(\delta^{34}S_{B}^{-} - \delta^{34}S_{A}^{-}\right)}{\left[SO_{4}^{2}^{-}\right]_{B}\left(\left[SO_{4}^{2}^{-}\right]_{A}^{-} - \left[SO_{4}^{2}^{-}\right]_{B}\right)} + \frac{\left[SO_{4}^{2}^{-}\right]_{A}\delta^{34}S_{A}^{-} - \left[SO_{4}^{2}^{-}\right]_{B}\delta^{34}S_{B}^{-}}{\left[SO_{4}^{2}^{-}\right]_{A}^{-} - \left[SO_{4}^{2}^{-}\right]_{B}^{-}}$$
(8)

where, $\delta^{34}S_n$ represents the sulfur isotopic composition in components A, B and mixture (M), and $[SO_4^{2-}]_n$ represents the molar fraction in components A, B and mixture (M). Fig. 7 shows a $\delta^{34}S-SO_4^{2-}$ vs. $Ln(SO_4^{2-})$ diagram with the mixing model between mine tailing waters and regional freshwaters developed using Eq. (8). Using this model, the mine tailing contribution in Zone 3, except for site ABQ-6, ranges between 45 and 80 % and in Zone 4 ranges from 5 to 25 %. These percentages agree with the calculated contributions using the Cl⁻ vs. SO_4^{2-} and $\delta^2 H vs. \delta^{18}O$ mixing models. This model has lower uncertainty to determine mine tailing contribution in Zone 3, due to the high sulfate concentration difference between freshwater and mine tailing water.

Finally, these three mixing models were also applied to groundwater and surface waters from Zone 5 (adjacent Cuncumén and Choapa Rivers, where extensive crops exist). Most of these samples lie in the regional freshwater area in the δ^2 H-H₂O and δ^{18} O-H₂O diagram (Fig. 5). In the δ^{34} S-SO₄²⁻ and δ^{18} O-SO₄²⁻ diagram, some Zone 5 samples could be explained as a mixing between mine tailings and regional freshwater, but most of them lie outside the mixing trend and could be explained by the contribution of sulfate from fertilizers (Fig. 6), considering also the lower SO₄²⁻ contents in these samples (between 19.7 and 68.8 mg L⁻¹). This hypothesis is confirmed with

the δ^{34} S-SO₄²⁻ vs. SO₄²⁻ model, as these samples divert from the mixing model between mine tailing waters and regional freshwaters (Fig. 7).

3.5. Water rights and effectiveness of hydraulic barriers

Upstream of the Quillayes TSF no alteration of the groundwater quality was observed, whereas a contaminated plume downstream to the TSF was identified (i.e., high conductivity and high dissolved sulfate, calcium, and chloride contents). The combination of hydrochemical and isotopic data used in this study confirmed that downstream groundwater was affected by mine tailing water seepage from the frontal dam of the Quillayes TSF.

This approach also allowed estimating the contribution of mine tailing water in the water mass pumped by the two hydraulic barrier wells, which were installed to intercept, mitigate, and remediate the potential mine tailing water seepage from the Quillayes TSF. The contribution of mine tailing water was estimated to be higher in the 1st hydraulic barrier (ABQ-9, ABQ-6C and ABQ-9A wells), between 45 and 90 %, than in the 2^{on} hydraulic barrier (ABQ-6-7A, ABQ-7, ABQ-7D and ABQ-8A wells), between 5 and 25 %. These results evidence the high effectiveness of the hydraulic barriers in intercepting contaminated water. Accordingly, the results point to no contribution of mine polluted waters in groundwater and surface water from Zone 5 (Cuncumén and Choapa Basin), located downstream to the 2^{on} hydraulic barrier (Figs. 5 and 7).

The wells installed as hydraulic barriers are subject to water rights and compute in the total water consumption right granted to the "Los Pelambres" mining company. However, water pumped in the hydraulic barriers is partially mine tailing water, which should not compute in the water rights. The estimated apportionment shows that pumped freshwater subject to water rights constitutes from 10 to 55 % of the water pumped in the 1st hydraulic barrier, except for ABQ-6 well, and between 75 and 95 % of the water extracted from the 2^{on} hydraulic barrier. Therefore, these results evidence how a proper pumping well design minimizes water rights



Fig. 7. Mixing model between SO_4^{2-} concentration and $\delta^{34}S-SO_4^{2-}$, showing mine tailing water (pink box) and freshwater (green box) end-members. Samples of groundwater collected downstream to the Quillayes tailing impoundment show $\delta^{34}S-SO_4^{2-}$ and SO_4^{2-} concentration that plot in the mixing area (orange box: 1st hydraulic barrier, zone 3; yellow box: 2^{on} hydraulic barrier, zone 4), whereas groundwater and surface waters obtained in crops along Cuncumén and Choapa rivers show $\delta^{34}S$ values and SO_4^{2-} compositions that departs from calculated mixing zone. GW: groundwater; SW: surface water.

consumption by mining companies. Nevertheless, the pumped water from the ABQ-6 well, which forms part of the 1st hydraulic barrier, corresponds 100 % to freshwater, indicating that this well is not effectively intercepting the contaminant plume and, therefore, all pumped water mass is subjected to consuming water rights.

To sum up, the multi-isotopic approach (δ^2 H-H₂O, δ^{18} O-H₂O and δ^{34} S-SO₄²⁻ and δ^{18} O-SO₄²⁻) used in this study allowed identifying and quantifying a decrease of mine tailing water contributions to groundwater downstream of the TSF, as well as determining the hydraulic barriers efficacy and quantifying the percentages of water rights consumed. With this study, we give a sound base on the application of these isotopic mixing models to mine tailing impoundments located at similar altitude than the source of process water used in the mine flotation plants.

For the shake of providing practical guidelines for further application to other mine tailing impoundments, the integrated method is summarized as follows. For an accurate quantification of the potential seepage from porphyry copper tailing impoundments, it is necessary to analyze δ^2 H and δ^{18} O of water, δ^{34} S and δ^{18} O of dissolved sulfate, and Cl⁻ and SO₄²⁻ concentrations from potential water end-members. The following potential water end-members should be considered: commonly regional freshwater (surface and groundwater) located upstream of the TSF, and polluted surface water stored in the tailing impoundment, which is subject to evaporation. To interpret the δ^2 H-H₂O and δ^{18} O-H₂O values of the considered end-members, it is important to define the Local Meteoric Line (LML) from rainwater isotopic data, and to calculate the theoretically Local Evaporation Line (LEL), according to equations presented in SI-4. The δ^2 H-H₂O and δ^{18} O-H₂O data projection will allow to identify potential water sources and occurring processes, as water evaporation or waters mixing.

For interpretation of S and O isotope data of dissolved sulfate it is also required to analyze the δ^{34} S-SO₄²⁻ and δ^{18} O-SO₄²⁻ of the end-members in porphyry copper mine tailings (sulfate and sulfur minerals). These values should be validated by comparison with the theoretical isotope ranges in the specific ore deposit site (if available). For a reliable interpretation of isotopic data from dissolved sulfate sourced from ore sulfide oxidation (pyrite, chalcopyrite, molybdenite, etc.), it is necessary to define the theoretical δ^{18} O-SO₄²⁻, which can be calculate according to equation developed by Van Stempvoort and Krouse (1994). The δ^{34} S-SO₄²⁻ vs. ln(SO₄²⁻) mixing model rather than the δ^{34} S-SO₄²⁻ vs. δ^{18} O-SO₄²⁻ model is more convenient for a precise quantification of sulfate sources.

Once the end-members are defined, the two mixing models (δ^{34} S-SO₄²⁻ vs. ln(SO₄²⁻) and δ^{2} H-H₂O vs. δ^{18} O-H₂O) are applied to samples collected from the pumping wells installed as hydraulic barriers to mitigate mine tailing water seepages from porphyry copper mine impoundment towards the neighboring groundwater. These samples will fit in a mixing zone defined by the considered end-members. By means of mixing calculations, the mass percentage of freshwater and polluted water in the pumping wells can be estimated. These quantifications allow also determining the percentage of water subject to water rights. The δ^{34} S-SO₄²⁻ vs. ln(SO₄²⁻) mixing model permits quantifying the water contribution in pumping wells installed far to the tailing impoundment, whereas the δ^{2} H-H₂O vs. δ^{18} O-H₂O model allows to calculate the polluted water percentage in pumping wells installed near the impoundment. Finally, these quantifications can be compared with those obtained from the Cl⁻ and SO₄²⁻ mixing model.

The multi-isotopic methodology presented in the current case study can be extrapolated to scenarios where the porphyry copper mine tailing impoundments are ubicated at the same altitude that the source of the process water used for the mining flotation. Thus, mine companies and public administrations could include the use of this multi-isotopic approach in this type of mine tailing impoundments to improve the decision making, by assessing and adjusting the design of hydraulic barriers and reducing the freshwater consumption from neighboring aquifers, with the consequent cost savings and environmental benefits. Nevertheless, further investigation is required for a widespread application of these tools for general mine tailing impoundments of other ore deposit type (skarn, epithermal, volcanogenic massive sulfide, among others), and particularly in scenarios where the porphyry copper mine tailing impoundments are located at different altitude than process water source.

4. Conclusions

In this study, a multi-isotopic approach has been applied for the first time to quantify the effectiveness of hydraulic barriers installed in mine tailing impoundments and the fraction of pumped water that is subject to water rights. Among the tracers used, δ^2 H and δ^{18} O of water and Cl⁻/SO₄²⁻ ratio were useful to quantify the contribution of freshwater in the pumping wells installed as hydraulic barriers to mitigate mine tailing water seepages from porphyry copper mine impoundment towards the neighboring groundwater. δ^{34} S and δ^{18} O of dissolved sulfate and δ^{34} S vs. ln(SO₄²⁻) mixing model were useful tracers when the opposite problem existed, i.e., pollution of fresh groundwater by mine tailing waters seepages. Consequently, the combined multi-isotope approach can be applied as a groundwater management tool in porphyry copper tailing impoundments to identify water and dissolved sulfate sources, as well as to quantify the contributions of mine tailing waters to groundwater, the effectiveness of installed hydraulic barriers, and the water rights that mining companies consume in the mitigation of contaminant plumes. This tool was applied in a case study where an impoundment that stores slurry tailings from a Chilean porphyry copper deposit is located at the same altitude than the source of the process water used for the mining flotation. The multiisotopic approach allowed identifying pumping wells that operate correctly, minimizing the contribution of water and dissolved sulfate from mine tailings, and those that are ineffective and do not intercept the contaminant plume and, they are therefore consuming water rights. This illustrates how a proper pumping well design could minimize water rights consumption by mining companies. Although further investigation is required in scenarios where the porphyry copper mine tailing impoundments are located at different altitude than the source of the process water, the proposed multi-isotope approach could be used by mine companies and public administrations to improve the decision making and the hydraulic barrier designs to reduce the freshwater consumption, as well as associated costs.

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Dídac Navarro-Ciurana: Conceptualization, Methodology, Resources, Formal analysis, Investigation, Visualization, Writing – original draft, Writing – review & editing. Agnés Saleta-Daví: Methodology, Resources, Formal analysis, Investigation, Writing – review & editing. Neus Otero: Investigation, Writing – review & editing. Clara Torrentó: Investigation, Writing – review & editing. Carlos Quintana-Sotomayor: Methodology, Resources, Writing – review & editing. Diego San Miguel-Cornejo: Methodology, Resources, Writing – review & editing. Mónica Musalem-Jara: Methodology, Resources, Writing – review & editing. Gullibert Novoa-Godoy: Methodology, Resources, Methodology, Writing – review & editing. Evelyn Aguirre-Dueñas: Project administration, Supervision, Resources. Manuel A. Escudero-Vargas: Resources, Methodology. Albert Soler: Project administration, Supervision, Investigation, Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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