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Research papers

Hydrogeochemical and environmental water quality standards in the overlap between high mountainous natural protected areas and copper mining activities (Mapocho river upper basin, Santiago, Chile)

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ABSTRACT

Natural hydrogeochemical backgrounds or signatures from rivers around the world show great differences depending on the geological and hydrological settings where the specific watershed is placed. This fact is especially relevant and notorious, when the metallic content of waters draining hydrothermally-altered high-mountainous regions is considered. The present study offers a hydrogeochemical perspective to improve the generation of Environmental Water Quality Standards (EWQS) in mineralized high mountain regions comprised by rivers unaffected and affected by acid rock drainage (ARD). To this end, the complex and versatile reality at the Mapocho river upper basin (comprised by a natural ARD affected sub-basin, a mining intervened sub-basin and a third sub-basin with Andean unaffected waters) was used to evaluate the effect of seasonal and long-term climatic variations on hydrothermally-altered high-mountainous regions.

In addition, 22 different environmental water quality standards (EWQS) from different countries around the globe were analyzed. This information was used to define what could be understood as “an acceptable water quality for environmental use”. Also, the obtained elemental concentration and physicochemical ranges were compared with the results obtained at the Mapocho upper basin to assess the importance of regional and local geochemical backgrounds on the generation of EWQS. As a result of this information generation, compilation, analyses and intercomparison, several recommendations to consider during the generation of EWQS at heterogenous high mountainous watersheds comprised by both ARD affected and unaffected sub basins were made. Special attention was paid to the incorporation of seasonal variations and long-term effects (climate change) on the generation of more realistic and useful EWQS.

1. Introduction

The mining industry is frequently associated with the degradation of environmental quality in terms of biodiversity (Murguía et al., 2016), water resources (Bellisario et al., 2013; Brenning, 2008; Caraballo et al., 2016; Wireman & Stover, 2011), soil (Pokhrel & Dubey, 2013) and air (ELAW, 2010), among others. There is a growing awareness and concern in both the scientific community and the general public about the occurrence of overlapping between mining properties and protected areas around the world (Armendáriz-Villegas et al., 2015; Durán et al., 2013). Assessing the mining industry-related impacts on the environment, especially on water quality, requires distinguishing between the natural geochemical background (pre-mining condition) and expected environmental conditions during the mining operation (including closure and post-closure stages). However, the best-case scenario in river basins around the world is to have very little (some years of limited hydraulic and hydrochemical records) or non-information of the natural geochemical background. This situation is even more critical for rivers in mountainous and remote regions, where many mining complexes are placed and can have decades of mining activity history. As a

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result, several authors have proposed alternative approaches to infer the natural geochemical background in watersheds affected by the mining activity with no previous hydrochemical or hydraulic records (Nordstrom, 2015; Runnells et al., 1992). These approaches are based on the comparison with a proximal analog watershed with a similar non-mined geological background and a strong hydrochemical and hydraulic record. It is also important to notice that although most mining projects around the world are required by law to present an environmental impact assessment (EIA), most cases actually underestimate water quality impacts due to the underestimation of the baseline water quality generated by their pre-mining conditions predictions (Kuipers et al., 2006).

Acid mine drainage (AMD) is recognized as one of the most serious environmental problems in the mining industry (Dold, 2017), because of its potential impact on water quality by inducing low pH and high electrical conductivity, sulfate and metals concentrations (Valente & Leal-Gomes, 2009). It is a common problem in all countries where mining started prior to any promulgation of an environmental legislation. In addition, when sulfide containing rocks reach the Earth surface, they naturally undergo a weathering process that, in the presence of water and air, typically lead to the generation of acid rock drainage (ARD) (Nordstrom, 2015; Verplanck et al., 2009; Williams et al., 2015).

The only difference between AMD and ARD is that the former implies some anthropogenic origin or enhancement whereas the latter has a natural origin. It is also important to realize that many high mountainous regions around the world (e.g., Andes, Himalayas, Alpes, Rocky Mountains, …) are characterized by the absence of soil and/or vegetation coverage, resulting on a geochemical signature of the waters that is predominantly due to the rocks of the region. Also, hydrometeorology is determinant to understand the extent, rate and seasonality of the final water quality generated. Since the specific characteristics of ARD (in terms of acidity and metal pollution) are mainly controlled by local geology and climatology, formulating site-specific water quality standards for ecosystems protection on these naturally occurring high acidity-high metal waters ought to be considered. It is important to bare in mind that ARD environments typically develop their own specific populations of metal-resistant species that have to be considered as the local normal ecosystem (Reimann & Garrett, 2005).

Generally speaking, global warming is expected to reduce snowfall and promote glacier retreat at high mountain regions (Huss et al., 2017; Sellami et al., 2015), uncovering bigger bedrock areas that will be exposed to aqueous weathering process, potentially increasing the appearance of ARD (Todd et al., 2012; Sharp & Tranter, 2017). On the other hand, it may also affect the hydraulic regime (Flores, et al., 2016), inducing lower water flows or changing the spatial distribution of the water courses. As a result, the specific long-term response to global warming of ARD at different high mountain hydrological systems may vary significantly. In addition, medium term climate fluctuations (e.g., long drought periods) may promote water-table depth decrease, and the concomitant increase of sulfide-bearing rocks submitted to surficial oxidizing environments. Thus, understanding the dynamical interaction between snowpack thickness, water-table depth, groundwater flow, bedrock mineral composition and surficial water flowrate at different time scales, is essential for water resources management in high-mountain environments affected by ARD or AMD.

In many countries around the world, water management frameworks include water supply oriented management for agricultural production and are progressing toward the incorporation of new management forms to regulate other water uses, address water quality issues and apply measures to control water demands (Grantham et al., 2013). In fewer cases, water management already considers a broader protection of the ecosystem processes and services, as it has been done for example by the European Water Framework Directive (European Communities, 2008). Despite this promising awareness of the importance of achieving a sustainable water management framework, the actual advance in this sense has been very limited in most countries (Gleick, 2014).

The present study explores the meteorological, hydrological and hydrochemical cycles of the upper Mapocho river basin (Santiago, Chile). This can be considered as a representative case of a complex high mountainous region comprised by three different sub-basins developed on the different geological sections of the hydrothermally altered rocks of one of the biggest porphyry Cu systems in the world. As a result of the different geological settings, hydrometeorological regimes and land uses, these three sub-basins cover almost all the specific water management situations typically appearing on those watersheds, namely: 1) a mining intervened basin with potential to generate AMD, 2) an undisturbed natural ARD, and 3) a non-metal polluted non-acidified river with high turbidity. The main scope of this study is to offer a hydrochemical perspective to create the necessary tools for the generation of environmental public policies in mineralized high mountain regions where mining activities are developed. In addition, the formulation of a secondary water quality standard for an environmentally sustainable use of these precious water resource in dry, semi-arid and arid regions is discussed. To this end, the suitability of the current Chilean “environmental water quality standard” (from now on, EWQS) is discussed to exemplify, with a real case, the complex geological, hydrometeorological, hydrochemical and anthropogenic interactions on these aquatic systems.

2. Field background information

2.1. Climate and hydrological context

The Mapocho upper basin is located east from the city of Santiago and comprises three main sub-basins: Yerba Loca, San Francisco and Molina, with areas of 189 Km^2, 108 Km^2, and 300 Km^2 respectively (Fig. 1). The basin emplaces from the low zones of the lower basin (966 m.a.s.l.) with temperate Mediterranean climate zone, to the high peaks of the Andes (about 4900 m.a.s.l.), where periglacial environment develops. Rainfall is mostly limited to winter months (i.e., May to September), with annual accumulated rainfall estimates on the range of 400–900 mm for altitudes above arboreal line (Figure A.1, Supplementary Information). Headwater zones of the Mapocho river have a snow-glacial character, during the dry season, the river is fed by: 1) snowmelting (more noticeable in Molina than Yerba Loca) and 2) glacier-defrosting, from both rock glaciers and “white glaciers” mostly at upper Yerba Loca basin. It is worth noting that the upper San Francisco basin (Fig. 1) have only little rock glaciers representing an almost negligible source of water. On the other hand, Mapochós lower basin has a pluvial character, being the Molina river the principal tributary of the Mapocho river, due to its bigger catchment area (Fig. 1).

This basal hydrometeorological regime has been altered (on its magnitude but not on its seasonality) since 2010 when a mega drought period was described for Central Chile (Garreaud et al., 2017). This mega drought extension and severity is unprecedented considering the records during the second half of 20th century. As a result, rainfall decreases, with an annual rainfall deficit ranging from 25 to 45%, and the subsequent substantial decrease of surface water resources are observed (Figure A.2, Supplementary Information).

2.2. Los Sulfatos deposit

The Los Sulfatos deposit is surrounded by a glacier system and is part of the Rio Blanco-Los Bronces copper-molybdenum porphyry district (yellow star in Fig. 1). This district is within the late Miocene to early Pliocene magmatic arc of central Chile, approximately 50 km northeast of Santiago at elevations between 3,000 and 4,800 m above sea level

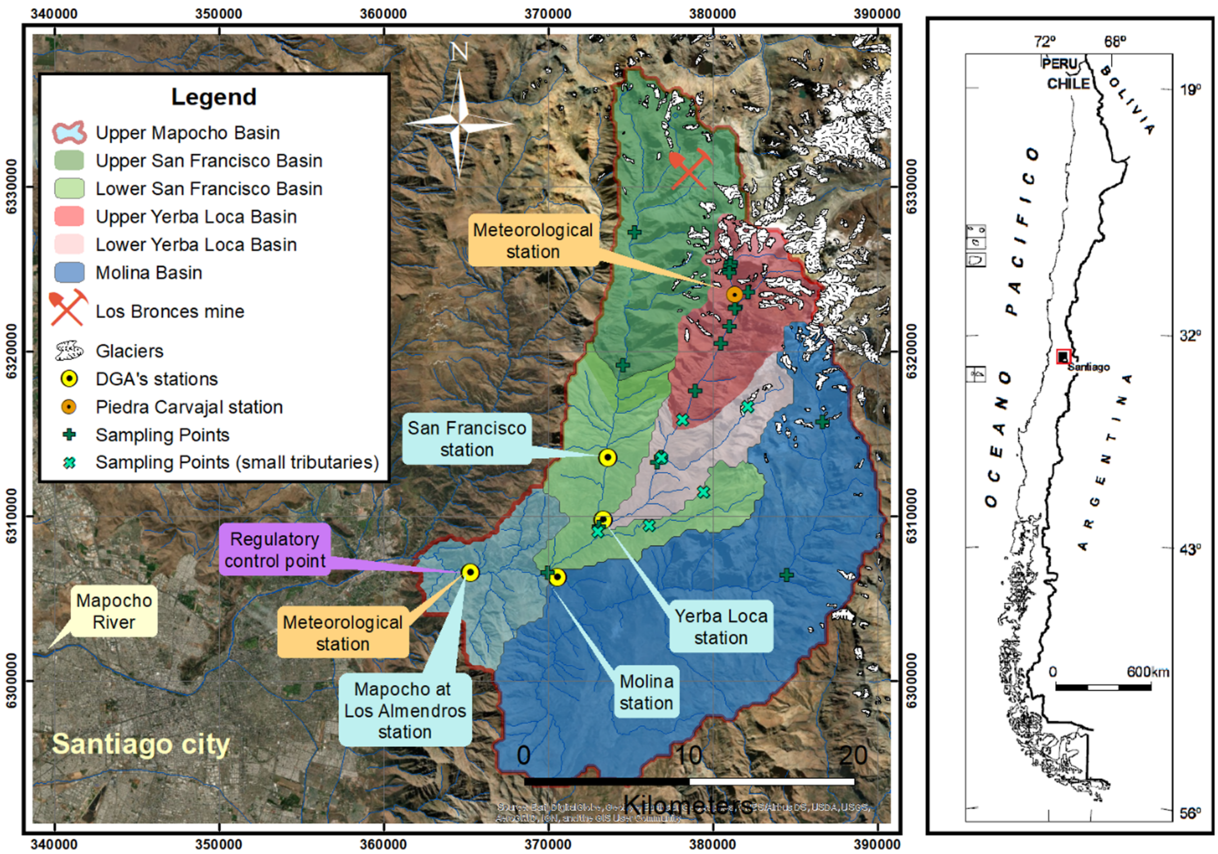

Fig. 1. The Mapocho river upper basin location map, indicating sub-basins, main rivers, main glaciers, DGA' stations, sampling points and the meteorological DGA's station at Piedra Carvajal.

(Toro et al., 2012). *Los Sulfatos* deposit comprises a large, multiphase, igneous/hydrothermal-cemented breccia complex, with at least two separate centers of porphyry copper-style mineralization (Toro et al., 2012). Locally cutting the breccia are sulfide-rich veinlets, containing pyrite-chalcopyrite at shallow levels and chalcopyrite-bornite at depth (Irarrazabal et al., 2010). Besides, at shallow levels and in the periphery, a pyrite (FeS_2) halo characterizes *Los Sulfatos* system (Toro et al., 2012). This district reports an inferred total resource of 206.7 Mt of fine copper (Toro et al., 2012), ranking it as the world's largest known copper concentration (Deckart et al., 2014; Irarrazabal et al., 2010; Toro et al., 2012). So, environmentally speaking, the abundance of sulfides in the area is the perfect scenario to generate ARD (Nordstrom & Alpers, 1999); whereas economically speaking, this mining district has become the world's greatest known deposit of copper and a potential increase in the productive development of the mine is expected (Medina, 2017).

2.3. *Chilean water management framework and Mapocho river upper basin*

Chile's strategy to develop a water market has facilitated water rights being transferred to uses with high monetary values. This situation has promoted economic efficiency, but at the same time it has failed to take into account environmental needs and values as well as human rights (Collins & Woodley, 2013; Jorquera et al., 2014). However, during the last years Chile is progressing towards an more integrated water management system (Grantham et al., 2013). The secondary EWQS was formulated locally for the Mapocho and the Maipo basins from 2003 to 2014 (Ministerio del Medio Ambiente, 2014). Headwaters in the upper San Francisco river have been vastly intervened by mining activities for more than 100 years (Toro et al., 2012). The Yerba Loca basin shows a natural low-pH environment in its upper section whereas in the lower basin is characterized by high seasonal variability of pH and metal concentrations records. This basin is almost unaffected by human activities (Gutiérrez et al., 2015; Jorquera et al., 2014) and was declared as "Nature Sanctuary" (a Chilean protection category) in 1973 (Ministerio de Educación Pública, 1973). Moreover, the Yerba Loca basin is regarded as biodiversity hotspot for conservation priority (Figueroa et al., 2013; Myers et al., 2000). Finally, the San Francisco and Yerba Loca rivers mix with the Molina river, which presents freshwaters unaffected by mining activities; and together originate the Mapocho river, which drains its water across Santiago city, with about six and half million-inhabitant population (approximately 40% of national population).

In addition, there is also an important socioenvironmental aspect that needs to be taken into consideration during the development of water management strategies for the region. Future underground exploitation of Los Sulfatos, partially developed underneath the Yerba Loca upper basin, is being considered. As a result, local and regional communities are paying special attention to any potentially negative outcome of this activity that could endanger the glaciers at Yerba Locás upper basin. Given the whole context, the water quality of the Mapocho river upper basin is scientifically, environmentally, socially and industrially relevant.

3. Materials and methods

3.1. *Water sampling and field measurements*

Historical data collection included a network of four stations with hydrological and hydrochemical monitoring in the Mapocho river

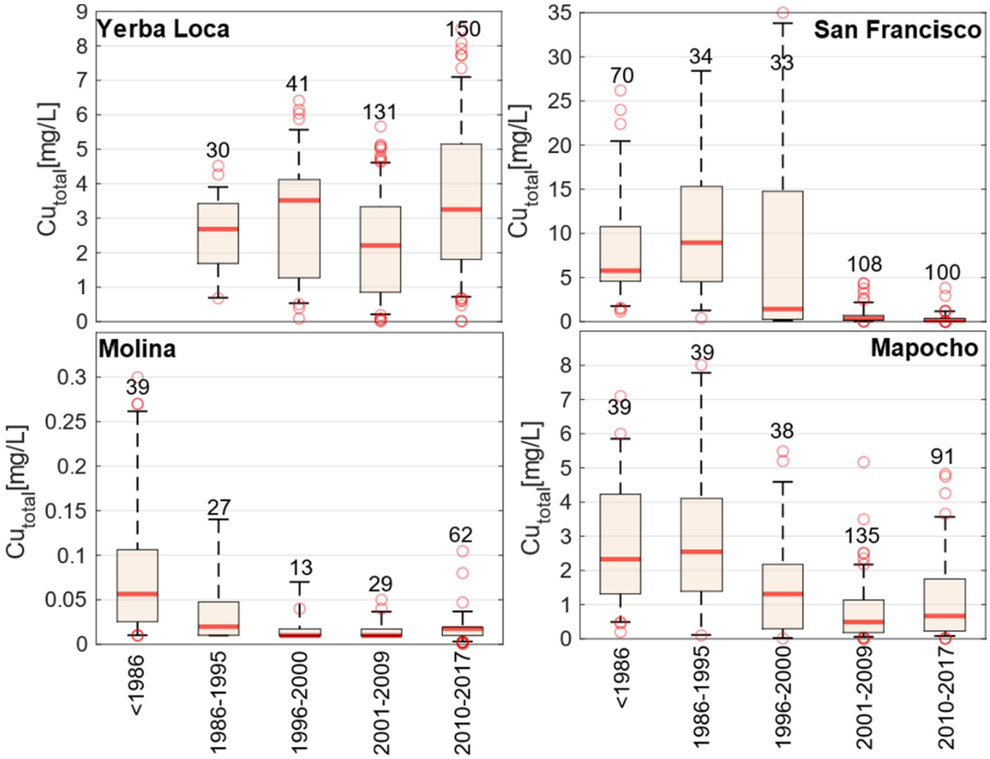

Fig. 2. Historical variations on Cu total concentrations in the Mapocho upper basin at DGA's stations. On each box declustered data distribution were plotted with their respective number of records. Red central mark indicates the median; bottom and top edges of the box indicate the 25th and 75th percentiles; whiskers extend to 5th and 95th percentile, and data out of this last range (outliers) are plotted individually using the red circles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

upper basin (Fig. 1) operated by the 'Dirección General de Aguas' (the Chilean water agency; DGA). Hydrochemical dataset include: 1) four samples per year for each DGA's station (650 samples) between 1974 and 2017; 2) several samples of the Yerba Loca, San Francisco and Mapocho rivers between 1998 and 2010 with monthly resolution; and between 2011 and 2017 with quarterly resolution, provided by Anglo-American to 'Servicio de Evaluación Ambiental' (the Chilean environmental assessment agency; SEA) (862 samples). 3) Another set of samples was obtained for the present research by different consulting companies and research institutes working on behalf of Anglo American (Los Bronces-mine Division). This additional database was made by 578 water samples (filtered and unfiltered samples) from the Mapocho river upper basin, 328 samples from the Yerba Loca river, from its headwaters to the mouth (until the confluence with the San Francisco river); and 250 samples from the San Francisco, Molina, Mapocho rivers and other small tributaries. These field samplings comprised from April 2013 to December 2017.

Hydrometeorological data set (Alvarez-Garreton et al., 2018) include: 1) streamflow for each DGA's station; 2) monthly mean temperature and monthly accumulated rainfall measured in the Yerba Loca river upper basin at Piedra Carvajal station (3250 m.a.s.l., Fig. 1); 3) monthly mean temperature and monthly accumulated rainfall measured in the Mapocho river at Los Almendros station (966 m.a.s.l., Fig. 1).

The location for of all sampling points (Table A.1) and hydro-meteorological stations (Table A.2), are available in the Supplementary Information.

3.2. Analytical methods

Water samples to study dissolved elements (consulting companies dataset) were filtered immediately at the field using 0.45 µm pore-size filters, collected in polyethylene bottles, preserved with HNO_3 to pH less than 1 and stored in coolers with ice packs to keep temperature close to 4 °C until arrival at the laboratory. Details about alkalinity, temperature, electrical conductivity, redox potential and pH field measurements were obtained *in situ*. Additional details can be found in the Supplementary Information.

Because the multiple sampling campaigns comprising the database were performed by different teams along the years, a variety of analytical techniques and instruments were used. On this regard, the samples obtained by the DGA were analyzed at its own laboratory, the samples obtained from SEA were analyzed at SGS laboratory, the ones obtained in the present study and by environmental consulting companies were analyzed by ALS or AcmeLab laboratories in Chile and Canada, respectively. Details of all the analytical procedures (Table A.3) and detection limits (Table A.4) used at the different sampling campaigns are described in the Supplementary Information.

3.3. Data QA/QC, analysis and consolidation

Data quality consolidation was performed through charge imbalance calculation for each sample using three different methods. Disaggregated (Table A.5, 6) and visual (Figure A.3 and Figure A.4) validation of the data comparing the different rivers and laboratories in the present study are shown in the Supplementary Information.

Typically, hydrochemical variables distributions (e.g., metals concentrations) are skewed, have outliers and are the result of different processes (Olsen et al., 2012). Therefore, irregular and time-scattered sampling data could generate biased estimators. Declustering algorithm (Chilès & Delfiner, 2012) with monthly cell resolution was considered to compute robust and unbiased estimators of location, spread and range limits for each variable (this method divides timeline in identical cells and assigns a weight inversely proportional to the number of data present in each cell). Median, MAD (median absolute deviation), 5th and 95th percentiles (instead of mean, standard deviation, minimum and maximum) were chosen like representative and robust estimators of water quality variables. Hydrochemical baseline of the Mapocho upper basin are shown in Table A.7 and Table A.8 (Supplementary Information) for each DGA stations in the studied period (2010–2017). Additionally, an extended Durov diagram was used as a graphical tool to show the hydrochemical processes occurring within the different hydrogeological systems (Al-Bassam & Khalil, 2012).

4. Results

4.1. Hydro-environmental characterization of the Mapocho upper basin

As suggested by Plumlee et al. (1999), copper can be considered a good indicator of ARD or AMD generation in watersheds draining Cu porphyry deposits. As a synthetic approximation to a more complex problem, the most relevant historical events affecting the Mapocho upper basin water quality are synthesized in Fig. 2. To this end, water samples from 1974 to 2017 were split into five different periods based on the following criteria: 1) before 1986, when sampling at Yerba Loca began; 2) 1986–1995, before any AMD remediation strategy was implemented at the San Francisco basin; 3) 1996–2000, from the beginning of the AMD remediation strategy implementation at the San Francisco basin until the year before the AMD remediation strategies had a discernible improvement effect on water quality (abrupt decrease in Cu concentration from over 30 mg/L to least 5 mg/L respect to former period, Figure A.5); 4) 2001–2009, when the AMD remediation strategies implemented in the San Francisco basin began to have a discernible improvement effect on the water quality and before the mega drought described for the central region of Chile (Garreaud et al., 2017); and 5) 2010–2017, length of the mega drought.

As shown by Fig. 2, copper concentrations in the Molina station are commonly lower than 0.1 mg/L and the calculated median values are typically lower than 0.03 mg/L. Therefore, this basin can historically be classified as non-affected by either ARD or AMD. On the other hand, the Yerba Loca watershed is characterized by median copper concentrations in the vicinity of 2.2–3.5 mg/L from 1986 to 2017. Thus, this basin can historically and consistently be classified as affected by ARD. As for the San Francisco basin, three different periods can be identified: a) before 1996 the river was clearly polluted by AMD with median Cu concentrations spanning 5 to 10 mg/L, b) from 1996 to 2000, Cu median concentrations decrease to 1.4 mg/L and showed a very high dispersion of the data; c) from 2001 to 2017, the outflowing are no longer affected by AMD. Finally, the samples corresponding to the Mapocho upper basin clearly reflect the combined history of the three sub-basins (Yerba Loca, San Francisco and Molina). The same line of reasoning can be obtained using water pH, with values lower than 5 marking the moments when San Francisco, Yerba Loca or Mapocho rivers behaved as AMD or ARD polluted waters (Figure A.5, Supplementary Information).

High mountain watersheds typically show complex hydrological regimes resulting from varying contributions of rainfall, snowmelt and glaciers melting throughout the year. On the one hand, these water sources are controlled by the regional climate; whereas on the other, they are expected to have a significant control on the hydrology and hydrogeochemistry of these basins along the years. The Central zone of Chile is considered a temperate Mediterranean climate and it is characterized by a wet season (May–October) and a dry one (November–April) (di Castri & Hajek, 1976). During wet season, the decrease of temperature coupled with the increase of rain allows the accumulation of snow above 0 °C isotherm in the three sub-basins (Fig. 3a). However, during storms, 0 °C isotherm can descend roughly to 2,200 m.a.s.l. covering with snow 60% of the basins, (or even 90% of the basins when 0 °C isotherm reaches 1,500 m.a.s.l., Figure A.1, Supplementary Information). Then, toward the end of the wet season, the increased energy loads in the upper zones induces snowmelt and increases the discharge of all rivers. This effect is more noticeable for the Molina river because of its bigger catchment area in the range of 1,500 to 2,500 m.a.s.l., (Figure A.1). Hence the Molina river (and as a result the Mapocho river) reaches its maximum discharge levels at the end of the wet season (i.e., blue lines at Fig. 3). On the other hand, during dry seasons, defrosting in the upper zones reach its maximum and 0 °C isotherm can raise even above 4,250 m.a.s.l. during summertime (Figure A.1). Thus, streamflow at Yerba Loca basin reaches its maximum because of its bigger catchment area over the glacier line (Figure A.1). As a result, Mapochós waterflow is generated by seasonally varying proportions of the Molinás and Yerba Locás discharges. The Molina river controls the discharge of the Mapocho river most of the year, providing almost 70% of its annual discharge; whereas the Yerba Loca river accounts for about 25% of Mapochós annual discharge. However, because Molinás and Yerba Locás discharge maximums are desynchronized, about 30 to 50% (or even more) of Mapochós discharge during dry months (Dec-Apr) can be supplied by the Yerba Loca

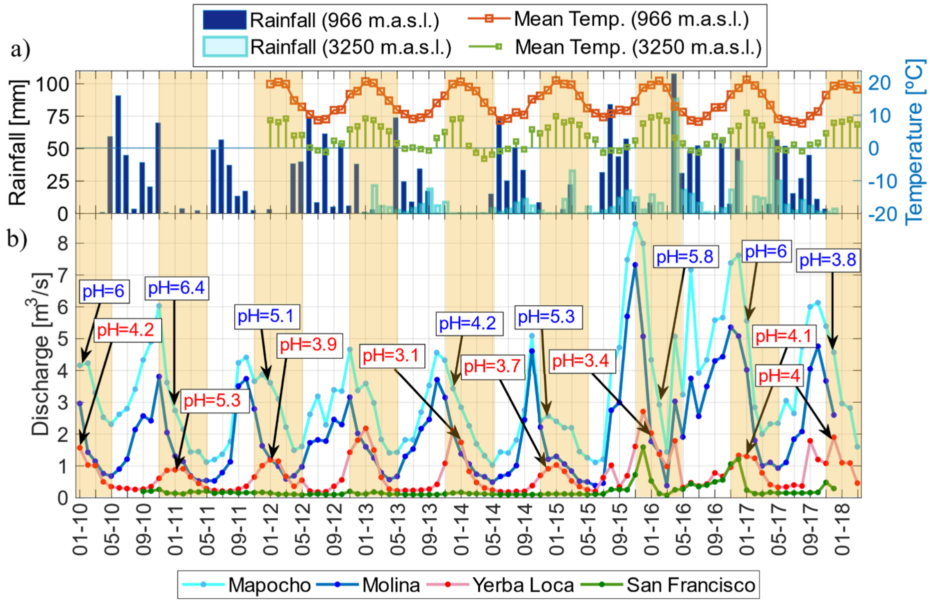

Fig. 3. Time series of monthly mean temperature, rainfall and streamflow values at DGA's from Jan-2010 to Mar-2018. Dry seasons are showed using transparent oranges boxes. a) Monthly mean values of temperatures and accumulated rainfalls at Mapocho's station (966 m.a.s.l) and Piedra Carvajal station (3,250 m.a.s.l.) b) Monthly mean values of flow discharges. The tags with pH values correspond to available samples on maximum discharges of Yerba Loca (in red) (Dec-Jan) and its repercussion over Mapocho (in blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

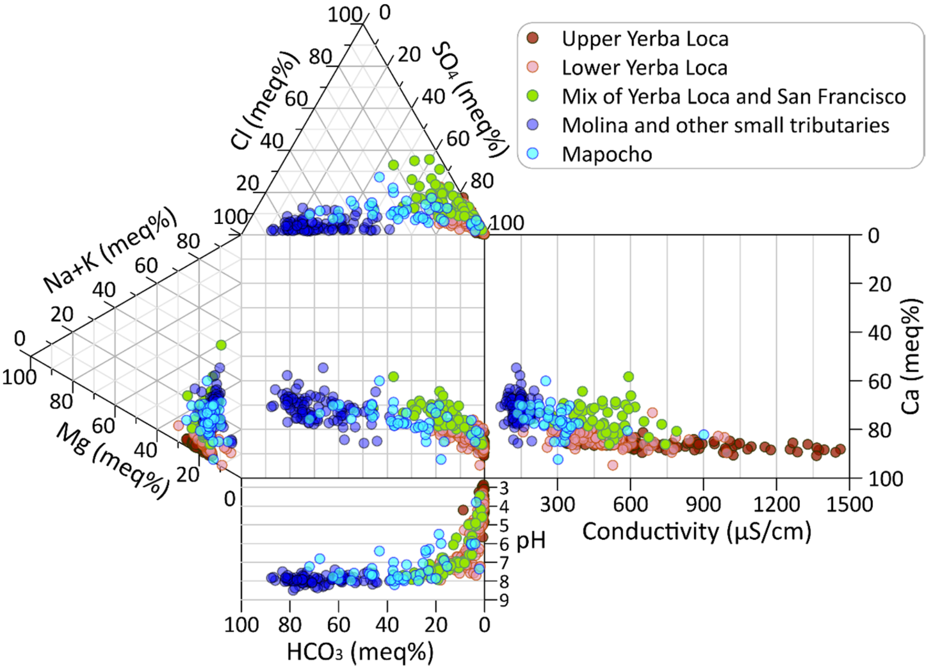

Fig. 4. Durov diagram of historical DGA's samples (2010–2017), 504 samples with complete records of major ions and physicochemical parameters.

river (Fig. 3). As a result, the Mapocho river frequently shows episodes along the year where it does behave as an ARD polluted river (i.e., low-pH values and significant concentrations of metals in solution). This situation has been accentuated during the dry years of the mega drought where the Molinás discharge has decreased relative to Yerba Locás discharge (e.g., Fig. 3b, hydrologic years 2011, 2012, 2013 and 2014). Please notice that the discharge of the San Francisco river remains low and almost constant through all the year because of the following reasons: 1) the existence of little rock glaciers, 2) its relatively small catchment and 3) its upper subbasin (Quebrada Disputada) is intervened by the mining activities, with the open pit generating a sump and a cut off wall in the waste rock dump, closing the upper Quebrada Disputada subbasin. Therefore, it typically provides less than 10% of Mapochós annual discharge, which doesn't match with its catchment area. For the sake of clarity, the following sections will mainly be focused on the relationship between the Molina and Yerba Loca rivers and their effect on the resulting Mapocho river. However, extended information about the San Francisco river is offered in the Supplementary Information.

Mapocho's upper basin hydrochemistry is graphically presented using an expanded Durov diagram (Fig. 4). As can be observed, the Molina river is characterized by calcium-carbonated waters with neutral pH and very low concentration of dissolved elements (representative specific elemental concentrations in Table A.7, Supplementary Information) and very low electrical conductivity (around 150 µS/cm). Headwaters of the Yerba Loca (Fig. 4) and San Francisco (Table A.7) rivers interact with very similar geological setting, resulting on similar major ion compositions. As a consequence, waters from both rivers upper basins can be classified as acidic and Ca-SO_4 type with relatively high conductivity and metals concentrations. In addition, waters from the upper zone of the San Francisco river (2600–2900 m.a.s.l.) are in close interaction with the mining activities and tend to include significant concentrations of Na and Cl, reflecting the salting of mine roads during winter (Jorquera et al., 2014). As mentioned before, the Mapocho river is mostly the consequence of different proportions of mixtures between the Molina and Yerba Loca rivers. Therefore, the specific percentage of mixture will control the hydrochemical signature of the river, making the composition of its waters to vary seasonally between Ca-SO_4 to Ca-HCO_3 types and its pH values from 5.2 to 8.6 (5%ile and 95%ile respectively, Table A.7).

A Ficklin diagram was used to classify the waters according to their metallic pollution and pH (Fig. 5). This type of diagram uses Zn, Cu, Pb, Cd, Co and Ni as fingerprints of ARD or AMD water pollution (Plumlee et al., 1999). As can be observed in Fig. 5, water samples from the Mapocho upper basin show a clear progression from acid waters with high metal content on one end (corresponding to most samples in the upper and lower basin of the Yerba Loca), to near neutral waters with low metal contents on the other end (due to the water samples from the Molina river). As a result of the mixture of these two end members, all the samples from the Mapocho river are located in between the three defined categories. Also is important to notice that the ARD at the upper Yerba Loca and the unaffected waters at Molina river can be classified as acid-high metal and near neutral-low metal respectively, through all the years (i.e., from 2010 to 2017, Fig. 5); whereas the lower Yerba Loca and Mapocho rivers fall into very different categories as a result of the seasonal and interannual variations of the waterflows and water qualities.

4.2. Water quality standards

The definition of suitable and site-specifics EWQSs should observe the current trends on water quality standards generation around the world as well as it should consider local geochemical background and hydrometeorology. To this end, guidelines values of 22 water quality regulations from different countries and or states/regions around the world (i.e., Argentina, Alberta, Australia, Brazil, British Columbia, Canada, Chile, China, Japan, New Mexico, Peru, Queensland, South Africa, Spain, Sweden, Switzerland, Texas, USA and European Union) were collected and analyzed (Table 1 and Fig. 6). Despite the existing differences between all these water quality regulations, all of them can be classified using two main categories: 1) Environmental, these type of regulations are intended to preserve water ecosystems and ecosystem

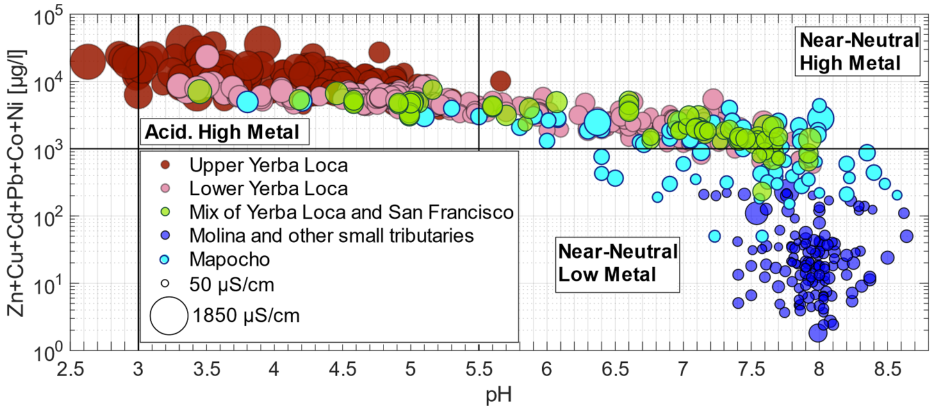

Fig. 5. Modified Ficklin diagram showing the sum of Zn, Cu, Cd, Pb, Co, and Ni total concentrations (n = 655 from 2010 to 2017). Circles relative sizes are proportional to samples electrical conductivity. Names defining the areas of the graphic are from Plumlee et al. (1999).

services through water quality maintenance or improvement (e.g. water for Wildlife and Livestock, chilean case); and 2) Aquatic Life, the main purpose of this type of regulations is to protect the most sensitive species and life stages against sub-lethal (chronic) and lethal (acute) concentrations of certain pollutant at different exposure times (Table 1).

At first glance, the generated database shows how most countries chose between having an Environmental-type regulation or an Aquatic Life-type regulation (Table 1). However, some countries/states with very recent regulations are choosing to follow both paths (i.e., British Columbia, Canada, 2018; New Mexico, USA, 2018 and 2017 and Peru 2017). Also, as a general pattern, Aquatic life water regulations show stricter limits (lower pollutants concentrations are allowed) than Environmental water regulations (Table 1 and Fig. 6). This pattern is clearly observed for NO_3^{2-}, Al, Cu, Zn, Cr, and Pb. On the other hand, pH, Cl, Fe, Mn, As and Ni concentration limits are very similar for both Aquatic life and Environmental regulations. Aquatic Life criteria are typically the most restrictive ones because most guidelines values are based on most sensitive species and life stage over a defined short-term exposure period (e.g. 96 h) so, dissolved concentration measurement is preferred (and recommended in most regulations) because this fraction better approximates bioavailable metals. On the other hand, Environmental guidelines values ranges are broader, reflecting that what is understood by 'an acceptable water quality for environmental use' is not clear and varies from region to region depending upon the regional predominant conditions (Fig. 6).

Also, it is important to notice that each country selects a specific set of elements/environmental parameters to be included in their water regulations. As a result, whereas some of them are included in most water regulations (i.e., pH, Cu, Zn, As, Cr, Ni and Pb), others are poorly or not included at all. Among the last, is worth noting the absence major ARD/mining-related elements (i.e., SO_4^{2-}, Fe, Al and Mn; Table 1). With the exception of Al, which is included in most Aquatic Life water regulations due to its toxicity (Tipping & Carter, 2011), the absence of other toxic elements is most probably to the fact that in most ARD-unaffected natural waters the concentrations of these elements tend to be very low and they don't represent a substantial risk for the environment. However, a few mg/L of these elements may induce severe ARD conditions and high toxicities (Nordstrom & Alpers, 1999).

5. Discussion

5.1. Evaluating the effect of long-term climatic variations on high mountainous watersheds affected by ARD

Droughts are likely to set in quicker and be more intense (Trenberth et al., 2014). The identified mega drought in Central Chile is consistent with the projected climate change for western subtropical South America (Garreaud et al., 2017). Despite water availability reduction being the principal impact of this mega drought, a detriment on water quality can be expected. To gain a better understanding of this issue, water quality indicators of the Yerba Loca and Molina rivers at DGA's stations were compared for the periods 2001–2009 (pre-drought period) and 2010–2017 (drought period) using statistical estimator ratios (Table 2).

'Median Index' (M.I.) and Range Index were obtained using the following equations:

$$M.\ I. = \frac{[X_{median}]_{(2010-2017)}}{[X_{median}]_{(2001-2009)}};\ R.\ I. = \frac{[X_{95th\%ile} - X_{5th\%ile}]_{(2010-2017)}}{[X_{95th\%ile} - X_{5th\%ile}]_{(2001-2009)}}$$

where X_{median} is the calculated median of a specific water quality parameter in the period 2010–2017 or 2001–2009, and $X_{95th\%ile}$ and $X_{5th\%ile}$ are 95th and 5th percentiles of a specific water quality parameter. Therefore, if an index is greater than one it indicates an increase of the median and/or range value for one parameter in the period 2010–2017 and vice versa.

The results in Table 2 clearly display an increase in the severity of the ARD at Yerba Loca during the drought period (2010–2017), showing lower pH and HCO_3^- concentration as well as higher electrical conductivity, hardness, SO_4^{2-}, Cu, Mn, As and Ni median values. Regarding water quality at Molinás basin before and during the drought period, and increase in SO_4^{2-}, K, Na, Al, Cu, Ni and Pb was observed. In terms of discharge, the mega drought has affected the Molina river harder than Yerba Loca river. This difference can be explained due to the size of their respective glacier areas that act as resilient systems, avoiding the Mapocho river to be without water throughout dry season.

5.2. The relevance of regional and local hydrogeochemical backgrounds on the generation of environmental water quality standards (exemplified at Mapocho upper basin, Chile)

Every watershed has a hydrochemical fingerprint inherit to the geochemical signature of the surrounding rocks. As a result of the specific regional and local lithology, waters at small basins comprising bigger watersheds may share a common regional geochemical background but also may exhibit their own local geochemical peculiarities. On this respect, waters from Yerba Loca and Molina basins share a regional geochemical background characterized by the presence of NO_3^-, Fe, As, Cr and Pb (Fig. 7); whereas the presence of low pH, and high electrical conductivity, SO_4^{2-}, Al, Cu, Mn and Ni is the specific local geochemical fingerprint of the ARD in Yerba Loca (Fig. 7). Finally, the Mapochós geochemical signature is a combination of the previous ones.

As a consequence, the generation of useful and realistic

Table 1
Water Quality Standards. Data are grouped in two different categories: Aquatic Life and Environmental.

		Alberta*		Argentina	Australia and New Zealand	Canada*	South African		Sweden*	Texas*		US	
		2018		1993	2000	2003	1996		2008	2018		2018	
		Aquatic Life (1)		Aquatic Life (1)	Aquatic Life (1)	Aquatic Life (1)	Aquatic Life (2)		Aquatic Life (2)	Aquatic Life (2)		Aquatic Life (2)	
	Unit	Acute	Chronic				Acute	Chronic		Acute	Chronic	Acute	Chronic
min. pH **	-	-	6.5	-	6.5	6.5	-	-	6	-	-	-	6.5
max. pH **	-	-	9	-	8.5	9	-	-	9	-	-	-	9
EC	µS/cm	-	-	-	350	-	-	-	-	-	-	-	-
DO***	mg/L	5	6.5	-	6	-	-	-	5	6	-	-	-
Cl	mg/L	640	120	-	400	120	-	-	-	-	-	860	230
NO_3	mg/L	124	3	-	17	13	-	-	-	-	10	-	-
SO_4	mg/L	-	310	-	1000	-	-	-	-	-	-	-	-
Al	mg/L	0.1(a)	0.05(a)	0.005	0.15	0.1	0.1	0.01	-	1	-	0.98	0.38
Cu	mg/L	0.016	0.007	0.002	0.0025	0.002	0.0016	0.00053	0.04	0.014	0.009	0.016	0.06
Fe	mg/L	-	0.3(a)	-	-	0.3	-	-	-	-	-	-	1
Mn	mg/L	-	-	0.1	3.6	-	1.3	0.37	-	-	-	-	-
Zn	mg/L	-	0.03	0.03	0.031	0.03	0.036	0.0036	0.3(e)	0.117	0.118	0.12	0.12
As	mg/L	-	0.005	0.05	0.36	0.005	0.13(d)	0.02(d)	-	0.34	0.15	0.34(d)	0.15(d)
Cr	mg/L	-	0.001	0.002	0.04	0.0089	0.34	0.024	-	0.016	0.011	0.57	0.074
Ni	mg/L	0.47	0.052	0.025	0.017	0.025	-	-	-	0.468	0.052	0.47	0.052
Pb	mg/L	-	0.0032	0.001	0.0094	0.001	0.004	0.0005	-	0.065	0.0025	0.065	0.0025

* Some guideline values were calculated using 100 mg/L as mean hardness.
** Guideline values indicate lower and upper thresholds.
*** Guideline values indicate lower threshold.
(1) Guidelines for the total metal concentration.
(2) Guidelines for the dissolved metal concentration.
(a) All metals are expressed in total concentration with exception of aluminum and iron.
(d) All metals are expressed in dissolved concentration with exception of arsenic.
(e) All metals are expressed in dissolved concentration with exception of zinc.

		British Columbia*		British Columbia	New Mexico*		New Mexico	Perú	Perú
		2018		2018	2018		2017	2017	2017
		Aquatic Life (1)		Environmental (1)	Aquatic Life (2)		Environmental (2)	Aquatic Life(1)	Environmental (1)
	Unit	Acute	Chronic	Wildlife and Livestock	Acute	Chronic	Wildlife and Livestock		Wildlife
min. pH **	-	6.5	-	6.5	6.6	6.6	6.6	6.5	6.5
max. pH **	-	9	-	9	9	8	8.8	9	8.4
EC	µS/cm	-	-	-	1500	1500	-	1000	5000
DO***	mg/L	5	8	-	5	6	-	5	5
Cl	mg/L	600	150	600	-	-	-	-	-
NO_3	mg/L	32.8	3	100	-	-	132	13	100
SO_4	mg/L	-	429	1000	-	-	-	-	1000
Al	mg/L	0.1 (b)	0.05 (b)	5	3.42(c)	1.37(c)	-	-	5
Cu	mg/L	0.011	0.004	0.3	0.013	0.009	0.5	0.1	0.5
Fe	mg/L	1 (b)	-	-	-	-	-	-	-
Mn	mg/L	1.64	1.05	-	3	1.6	-	-	0.2
Zn	mg/L	0.04	0.015	2	0.16	0.121	25	0.12	24
As	mg/L	0.005	-	0.025	0.34	0.15	0.2	0.15	0.2
Cr	mg/L	-	-	-	0.016	0.011	1	0.011	1
Ni	mg/L	-	-	-	0.47	0.052	-	0.052	1
Pb	mg/L	0.082	0.0065	0.1	0.065	0.003	0.1	0.0025	0.05

* Some guideline values were calculated using 100 mg/L as mean hardness.
** Guideline values indicate lower and upper thresholds.
*** Guideline values indicate lower threshold.
(1) Guidelines for the total metal concentration.
(2) Guidelines for the dissolved metal concentration.
(b) All metals are expressed in total concentration with exception of aluminum. Guideline of acute dissolved iron (0.35 mg/L) also is considered.
(c) All metals are expressed in dissolved concentration with exception of aluminum.

		Brazil	Chile	China		Japan	Spain	Queensland	Switzerland		UE
		2005	2014	2002		2003	2011	2005	2011		2008
		Environmental (1)	Environmental (2)	Environmental		Environmental (1)	Environmental (2)	Environmental (1)	Environmental		Environmental (2)
	Unit		Wildlife and Livestock	Type I (best)	Type V (worst)				Dissolved	Total	
min. pH **	-	6	6.5	6	6	6.5	-	6.8	-	-	-
max. pH **	-	9	8.5	9	9	8.5	-	9.5	-	-	-
EC	µS/cm	-	400	-	-	-	-	-	-	-	-
DO***	mg/L	6	8	7.5	2	7.5	-	4	-	-	-
Cl	mg/L	250	30	-	-	-	-	-	-	-	-
NO_3	mg/L	10	1.5	10	25	-	-	100	-	-	-
SO_4	mg/L	250	150	-	-	-	-	-	-	-	-
Al	mg/L	0.1(f)	-	-	-	-	-	-	-	-	-
Cu	mg/L	0.09(f)	-	0.01	1	-	0.12	0.006	0.002	0.005	-
Fe	mg/L	0.3(f)	-	0.3	-	-	-	0.5	-	-	-
Mn	mg/L	0.1	-	-	-	-	-	0.01	-	-	-
Zn	mg/L	0.18	0.03	0.05	2	0.03	0.5	0.06	0.005	0.02	-
As	mg/L	0.01	-	0.05	0.1	-	0.05	0.05	-	-	-
Cr	mg/L	0.05	0.05	0.01	0.1	-	0.05	0.1	0.002	0.005	-
Ni	mg/L	0.025	0.02	0.02	0.02	-	0.02	0.04	0.005	0.01	0.02
Pb	mg/L	0.01	0.007	0.01	0.1	-	0.0072	0.03	0.001	0.01	0.0072

** Guideline values indicate lower and upper thresholds.
*** Guideline values indicate lower threshold.
(1) Guidelines for the total metal concentration.
(2) Guidelines for the dissolved metal concentration.
(f) All metals are expressed in total concentration with exception of aluminum, copper and iron.

environmental water quality guidelines on these geologically heterogeneous high mountainous watersheds must recognize and include these hydrochemical singularities. As shown in Fig. 7, if the same water quality limits are applied to all the waters comprising the Mapocho upper basin (red lines in Fig. 7 correspond to the current Chilean guidelines values), the naturally occurring concentrations of some elements at Yerba Loca would be considered as water pollution (e.g., electrical conductivity, SO_4^{2-} and Zn). A similar situation is observed if the range of international environmental water limits (green areas) is considered. Notice that even using the most flexible and less strict limits in some international regulations (upper section of the green areas), the natural concentration of some elements would still be considered as pollution (i.e., Al, Cu, Fe and Mn).

On the other hand, the use of the same water quality limits for all the waters at the Mapocho upper basin would imply that the Molina basin is over regulated. As a consequence, there would be a significant margin for some elements to increase their water concentration before triggering a pollution alarm. Using Cu as an example, this element concentration at Molinás water is typically lower than 0.05 mg/L, whereas the concentration at Yerba Locás waters is commonly lower than 5 mg/l (95th percentile was used in both cases). If the worst-case scenario is used to generate a single water quality limit for the whole

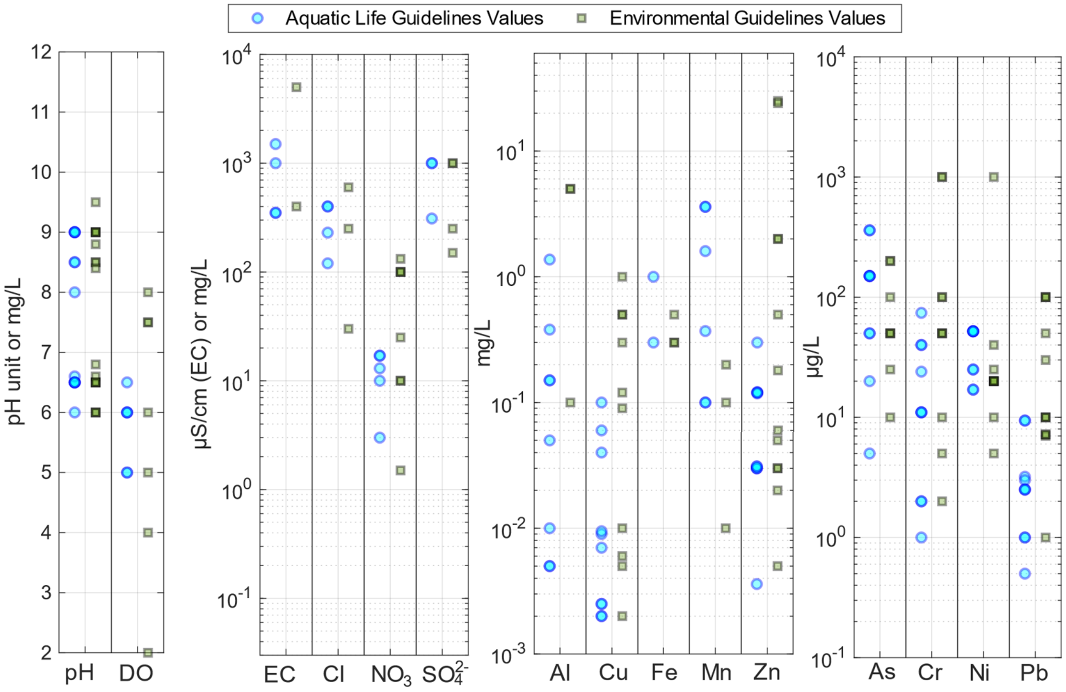

Fig. 6. Water quality standard values for aquatic life and environmental guidelines in 15 countries and 5 provinces/states around the world. Notice that individually plotted data for different countries may coincide and therefore are represented in the exact same position on the graphic (i.e., 4 different countries limit As concentration, according to their aquatic life guidelines, to 0.15 mg/l).

Table 2
Hydrochemical comparison between 2001 and 2009 and 2010–2017 periods at DGA's stations. M.I. = Median Index and R.I. = Range Index calculated using data from periods 2001–2009 and 2010–2017 as explained in the main text.

	Yerba Loca		Molina	
	M. I.	R. I.	M. I.	R. I.
Discharge	**0.68**	0.56	**0.47**	0.38
pH	**0.92**	1.18	1.02	0.89
EC	**1.15**	1.06	1.1	2.49
Temp.	0.87	0.92	0.92	1.17
Ca	1.22	0.94	1.16	0.91
Mg	1.12	1.01	1.25	1.82
Hardness	**1.47**	0.77	1.18	0.96
Na	1.22	0.36	**1.3**	1.33
K	1.21	1.29	**1.39**	0.41
HCO_3	**0.22**	0.61	0.97	0.72
Cl	1.07	0.63	1.15	0.85
SO_4	**1.47**	0.98	**1.62**	1.29
Al	1.11	1.74	**1.3**	0.26
Cu	**1.43**	1.44	**1.51**	0.82
Fe	0.88	2.86	0.82	0.74
Mn	**1.3**	1.4	0.66	0.76
Zn	0.9	1.73	0.97	0.69
As	**1.49**	1.77	0.95	0.47
Ni	**1.26**	1.74	**2.11**	2.98
Pb	0.73	1.59	**5.19**	1.73

Mapocho upper basin, Cu concentration at Molinás waters could increase up to two orders of magnitude before it can be considered a pollution. Other approaches has dealt with similar situation using a qualitative "Water Quality Index", without the need of set threshold values for each sub-basin. However, they have the limitation of not highlighting the parameter(s) that exceed threshold values (Espejo, et al., 2012).

6. Conclusions

On the basis of the experience gained during the generation of the hydrogeochemical background at Mapocho upper basin (Table 3) and the comparison with local and international Environmental Water Quality Guidelines, the following considerations may be issued when generating a Local Environmental Water Quality Guideline at heterogenous high mountainous watersheds comprised by both ARD affected and unaffected sub basins:

1) All major elements involved in the specific water–rock interactions controlling the water chemistry must be included. The specific elements to consider will depend upon the regional and local lithology, but at least the following elements should be included: Al, Ca, K, Mg, Na, Si and HCO_3 (as typical rock forming elements), Cl, PO_4^{3-} and NO_3 (as common inorganic pollutants), SO_4^{2-}, Cu, Fe, Mn and Zn (as common ore forming major elements) and As, Cr, Ni and Pb (as common ore forming minor elements).
2) Based on the results of the present study, hydrochemical backgrounds (comprised by water samples obtained on a monthly basis) may highly differ depending on the extension of the studied period and on the specific sub-basin. This information is essential to define efficient regulations covering the inherent spatial and temporal heterogeneities of these high mountaneous systems. When possible, it is recommended to obtain several years of information (five years could be considered as adequate but ten years may be needed).
3) The possibility of water quality seasonal variations should be acknowledged and included in the regulatory limits if applicable. As an example , the Yerba Loca sub-basin shows significantly different representative upper thresholds between wet and dry seasons, whereas Molina sub-basin does not (Table 3).
4) To enforce any Local Environmental Water Quality Regulation, at least a monthly sampling program should be required. If concentrations are steady and rarely exceed the upper thresholds

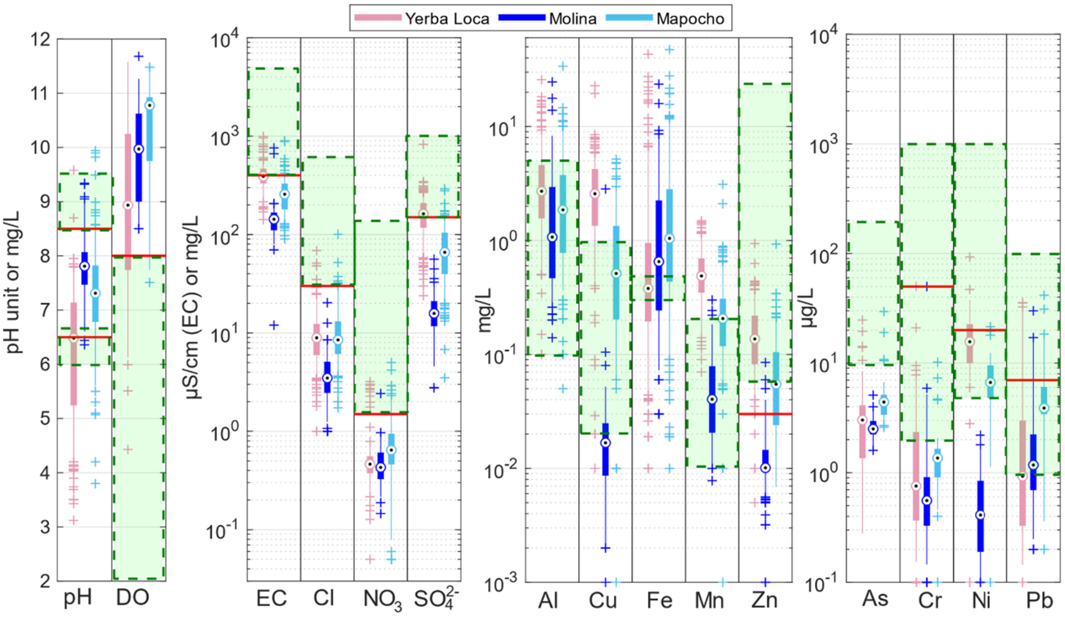

Fig. 7. Comparison between Mapocho, Yerba Loca and Molina elemental concentrations of water chemistry parameters at DGA's stations (2001–2017); current Chilean guidelines values (red lines) and international Environmental water limits (green areas). Declustered data distribution are plotted. Central circle indicates the median; bottom and top edges of the box indicate the 25th and 75th percentiles and whiskers extend to 5th and 95th percentile. Data out of this last range (outliers) are plotted individually using '+' marks. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

Hydrogeochemical background of the different sub-basins comprising the Mapocho upper Basin. 95th percentiles are shown as representative statistical values of the upper thresholds naturally observed at the basins. Notice that pH and DO values correspond to 5th percentiles shown the lower thresholds.

		YERBA LOCA		SAN FRANCISCO	MOLINA	MAPOCHO	
		Dry Season	Wet Season	Annual	Annual	Dry Season	Wet Season
pH	-	3.5	5.2	6.2	7.2	4.2	6.7
EC	μS/cm	716	506	936	391	500	331
DO	mg/L	5.1	6.1	5.5	8.5	9.2	7.5
Cl	mg/L	21	14	95	11	29	30
NO_3	mg/L	1.72	0.78	3.54	0.91	2.11	2.9
SO_4	mg/L	319	218	280	32	175	96
Al	mg/L	16.1	6.4	2.6	4.5	11.1	9.4
Cu	mg/L	7.6	5.5	1.2	0.04	3.8	0.87
Fe	mg/L	20	3.4	2.6	7.2	14.1	10.3
Mn	mg/L	1.4	0.73	0.77	0.19	0.8	0.33
Zn	mg/L	0.41	0.2	0.32	0.03	0.24	0.1
As	μg/L	14	7.7	12	3.9	11	5.1
Cr	μg/L	8.8	3.4	8	5	4.7	1.5
Ni	μg/L	42	20	11	2	20	7
Pb	μg/L	32	10	18	16	16	18

EC, specific conductance; DO, dissolved oxygen.

(Table 3), less frequent monitoring may be justified (e.g. Molina river). On the contrary, continuous online measurements of some selected parameters (i.e., pH and conductivity for ARD affected waters) is advisable when the sub-basin is expected to show important water quality variation in short periods of time (e.g., daily or seasonal variations).

5) Based on the expected variations resulting from the effect of Climate Change on these high mountain regions, the generated Environmental Water Quality Guideline must be revised every few years, on the light of the new data collected, to adjust the regulatory limits.
6) This historical knowledge is essential to implement realistic EWQS incorporating the regional and local hydrogeochemical signature as well as possible climate change effects (e.g., mega droughts). This detail knowledge will avoid unnecessary socio-environmental misunderstandings and conflicts in natural areas where the presence of mining activities is common or expected.

CRediT authorship contribution statement

Martín J. Valenzuela-Diaz: Conceptualization, Formal analysis, Investigation, Methodology, Writing - original draft, Writing - review & editing. **Alvaro Navarrete-Calvo:** Methodology, Formal analysis, Writing - review & editing. **Manuel A. Caraballo:** Conceptualization, Investigation, Supervision, Validation, Writing - original draft, Writing - review & editing. **James McPhee:** Funding acquisition, Project administration, Validation, Writing - review & editing. **Andreina Garcia:** Funding acquisition, Project administration, Writing - review & editing. **José Pablo Correa-Burrows:** Methodology, Formal analysis, Writing - review & editing. **Leonardo Navarro-Valdivia:** Methodology, Formal analysis, Writing - review & editing.

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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