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Surface water quality in a sulfide mineral-rich arid zone in North-Central Chile: Learning from a complex past, addressing an uncertain future

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Abstract

This study presents an analysis of up to 30 years of hydrological variables and selected water quality parameters (pH, SO_4, Fe, Cu, and As) in the upper area of the Elqui River basin in North-Central Chile. A correlation analysis determined statistically significant positive relationship for SO_4-Cu, Fe-As, and Fe-Cu. In terms of historical behaviour, no statistically significant trends were detected for precipitation or temperature. In contrast, for flow, there is an overall decreasing pattern for the entire area of study, although only in one case this trend was statistically significant. Along with the aforementioned analysis, a characterization of the flow-water quality relationships is considered for the time period analyzed. Although erratic behaviours were confirmed, a negative (i.e., inverse) flow-concentration relationship was identified for SO_4, a positive (i.e., direct) relationship for Fe, and undefined relationships for As and Cu were obtained. From these analyses and based on previous studies on projections regarding climate change for the Andean region, and in particular for the upper Elqui zone, an estimation of the possible effects of the change in water regimes on water quality in the area of study is developed. It is likely that a decrease in surface flow, as a consequence of climate change could translate into improvements in water quality in terms of Fe and eventually As and Cu, but into an impairment in the case of SO_4. In any case, this is a complex situation that demands special attention in the face of industrial activities that could be developed in tributaries like the Claro River, which currently play an important role in depurating or diluting contaminants in the waters of the Elqui River. Finally, it should be noted that this study addresses an issue that goes beyond the local interest and could be used as a reference to compare other transitional environments containing sulphide ores or areas of hydrothermal alterations, which are considered to be highly vulnerable to climate change and variability.

KEYWORDS

acid rock drainage, Andean river, arid zone, Coquimbo region

1 | INTRODUCTION

Water contamination as a result of acid rock drainage (ARD), whether from rock outcrops with high content of sulfide minerals or with hydrothermal alteration, or from mining sites, is a significant problem in various mining regions across the world (Pizarro, Vergara, Rodríguez, & Valenzuela, 2010; Todd et al., 2012). In fact, ARD has been recognized by the United States Environmental Protection Agency as "one of the three top ecological-security threats in the world" (Dold, Wade, & Fontboté, 2009).

Along with geologic aspects, there are climatic factors that can directly or indirectly influence the generation of ARD, the metal and metalloid dispersion, as well as the extension of associated water contamination problems (Munk, Faure, Pride, & Bigham, 2002; Nordstrom, 2011; Todd et al., 2012). For example, oxidation reactions involving

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sulphide minerals are dependent on the environmental temperature, which affects the bacterial activity associated with the generation of ARD. Also, local hydrology and flow patterns, which are a consequence of local climate and geology, control the sub-superficial distribution of water and oxygen as well as the transport of weathering products (Munk & Faure, 2004). Similarly, glacier retreat may expose underlying bedrock zones with lithology rich in sulphide minerals (Fortner et al., 2011). Furthermore, warmer temperatures can increase evapotranspiration, affecting recharge rates and water table levels, leading to a larger subsurface rock volume that interacts with oxygen, and therefore, allowing more sulfide oxidation (Mast, 2013).

Although there is abundant literature on the impact of climate change/climate variability on the hydrological behaviour of river basins (e.g., Bartnett, Adam, & Lettenmaier, 2005; Leavesley, 1994; Milly, Dunne, & Vecchia, 2005), the effects on water quality have been studied to a much lesser degree (Glavan, Ceglar, & Pintar, 2015; Kundzewicz et al., 2008; Rehana & Mujumdar, 2011; Van Vliet & Zwolsman, 2008; Whitehead, Wilby, Battarbee, Kernan, & Wade, 2009). Nonetheless, it is interesting to note the work of Whitehead et al. (2009), which presents an overall summary of the probable effects of climate change on different pollutants, with a focus on the United Kingdom. Similarly, and under a rather broader approach, Depla, Jung, Barnes, Clement, and Thomas (2009) present a literature review on the impact of climate change on surface water quality, considering diverse types of contaminants (e.g., dissolved organic matter, nutrients, inorganic contaminants and pathogens), emphasizing the effects on drinking water. In terms of climate change and the generation of ARD, Nordstrom (2009) developed a study in three basins in the USA, mainly focused on transient, flush-out events linked to the first episodes of precipitation after the dry season. However, studies related to the potential long-term effect of climate modification over local hydrological processes affecting the presence of heavy metals in waters of basins with mining activities or with natural factors predisposing the generation of ARD are generally lacking (Nordstrom, 2011). One of the few studies on these issues was conducted by Todd et al. (2012), who analyzed a 30-year stream water chemistry data set in the small (approximately 12 km^2) Snake River watershed, in central Colorado's Rocky Mountains. However, when specifically considering the case of arid zones with mining activity, it is fair to say that the understanding of the potential effects of climate change on water quality is even less.

Furthermore, and to the best of our knowledge, an integration of historical information regarding water quality, addressing the relationship between past climate variability and the potential future effects of climate change on water quality as a consequence of hydrological changes, has not yet been performed in Chile, despite the fact that the country is already facing serious water availability restrictions and exhibits an active, globally significant mining industry (Oyarzún & Oyarzún, 2011). This has even greater relevance when one considers that an important part of Chilean mining activities are developed in Andean range basins ("alpine" basins), which could be particularly susceptible to environmental disturbances, as well as to climate changes (De Maria, Maurer, Thrasher, Vicuña, & Meza, 2013; Todd et al., 2012). Even more, mining sites are largely located in the north central region of the country, where environmental conditions are arid and semi-arid, making them still more vulnerable to potential climate modifications and their subsequent effect on water regimes, and eventually, water quality.

The Elqui River basin, located in the Coquimbo Region, North-Central Chile (Figure 1), provides an interesting and useful study case. In fact, the catchment exhibits natural characteristics favourable for ARD generation (i.e., high sulfidation mineralization zones and extensive areas of advanced argillic alteration), as well as a significant history of mining activity, which have contributed to the presence of heavy metals, in specially high levels, both in surface water and sediments (e.g., Oyarzun, Lillo, Higueras, Oyarzún, & Maturana, 2004; Oyarzun et al., 2006; Oyarzún et al., 2013; Pizarro et al., 2010). Additionally, in the basin, there are rivers with excellent water quality that play both a purifying and diluting role (Espejo et al., 2012), the former due to the effect of increasing pH resulting in the formation of oxyhydroxides that sorb base metals, and the latter as a consequence of the mixing of waters containing different levels of pollutants (as is the case for SO_4 and As). These natural regulation mechanisms could be affected by climate change and the subsequent effect on the main hydrological processes. Furthermore, the Elqui basin is characterized as a snow-dominated basin, which would make the area especially susceptible to any change in the proportion of precipitation falling in the form of rain and snow, and for the latter, to accelerated rate of melting as a result of an eventual warmer climate (De Maria et al., 2013). Finally, in spite of the arid to semi-arid regime of the basin, there is a prosperous agricultural activity aimed for exportation that covers approximately 23,000 ha, mostly in the middle and lower areas of the Elqui basin, which is sensible to changes in water quantity and quality.

Within this framework, this study has three aims: (a) to characterize trends in hydro-meteorological variables (temperature, precipitation, and flow) and concentrations of selected parameters of environmental interest (SO_4, As, Cu, and Fe) in the upper area of the Elqui basin; (b) to determine the water flow/water quality relationship for each parameter considered; and (c) to use the obtained results, along with the existing literature, to assess possible changes in water quality as a result of climate change/climate variability in the basin. The results obtained in this study should be of interest in other similar mountain range basins in arid and semi-arid regions having contamination problems associated to lithological (i.e., natural) factors or mining activity, and facing likely water regime changes as a consequence of predicted climate modifications.

2 | STUDY AREA

The Elqui River basin is located in North-Central Chile (Figure 1), covering an area of approximately 9,850 km^2 (Espejo et al., 2012; Galleguillos, Oyarzún, Maturana, & Oyarzún, 2008). The upper, eastern area of the basin (andean zone), where the current study was conducted, exhibits narrow valleys and is mainly made up of igneous rock massifs, with the highest summits exceeding 5,000 m, with a mean slope of 24° (Oyarzun et al., 2006; Souvignet, Gaese, Ribbe, Kretschmer, & Oyarzun, 2010).

In terms of the climate, the inland pre-mountain zone is the most arid, with a relative humidity not exceeding 20% on hot days, absence

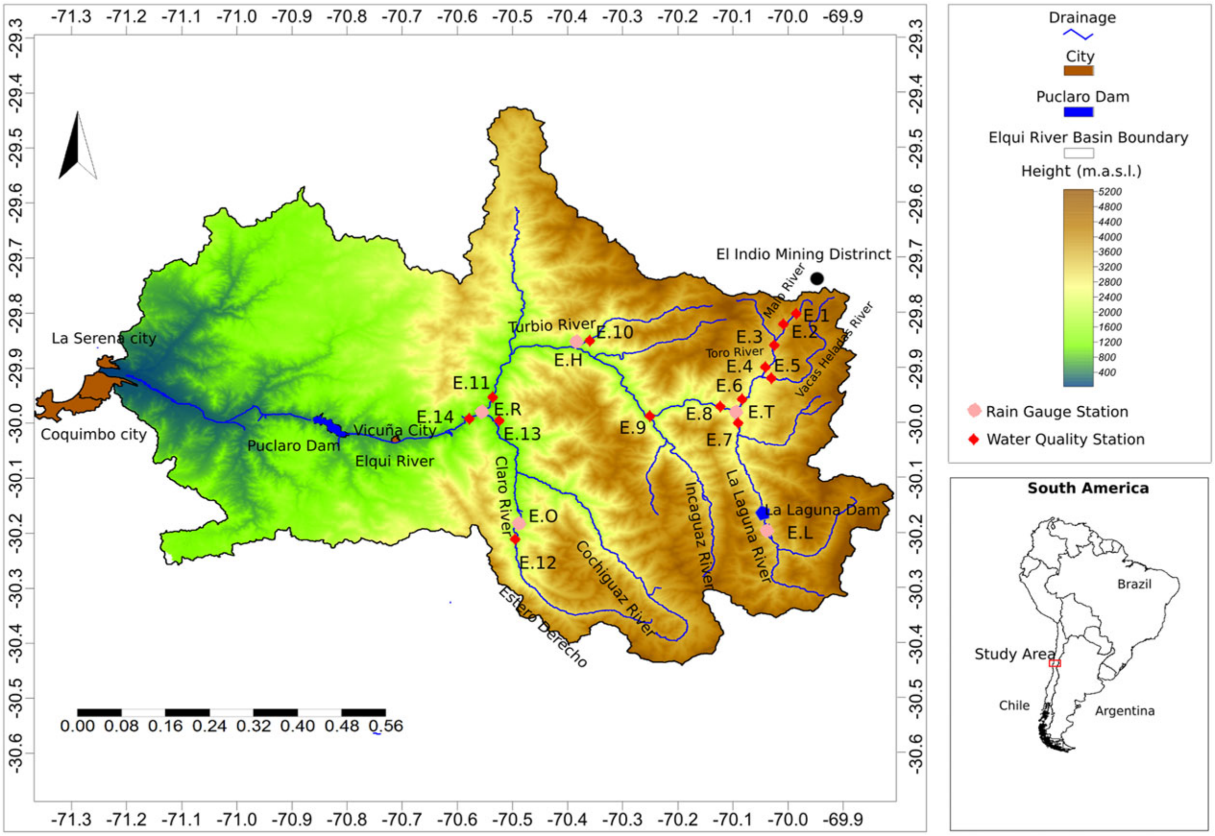

FIGURE 1 Elqui River basin, main tributaries and location of meteorological, flow and water quality stations considered in the study

of cloud cover and a daily thermal oscillation that can attain ~20°C in summer. The upper region of the basin exhibits a mountainous semi-arid climate, with minimum annual temperatures of approximately −15°C, frequent strong winds and precipitation mainly in the form of snow (Fiebig-Wittmaack, Pérez, & Lazo, 2008). The annual precipitation shows a strong orographic dependence, reaching some 300 mm/year in the Andes mountains (Favier, Falvey, Rabatel, Pradeiro, & Lopez, 2009). Major controls for precipitation events, in addition to the altitude, are the 5–7 year return period of the El Niño-Southern Oscillation phenomenon, which includes extremely rainy years (El Niño) and extremely dry ones (La Niña), as well as long term changes associated with the Pacific Decadal Oscillation (Núñez, Rivera, Oyarzún, & Arumí, 2013).

The fluvial network of the upper basin is formed by six main rivers (Toro, La Laguna, Turbio, Incaguaz, Claro, and Elqui), and three minor ones (Vacas Heladas, Malo, and Estero Derecho). Snow plays in general a major role in the basin's hydrology (Souvignet et al., 2010), while glaciers may be significant contributors to surface discharge in years with low precipitation, although their surface coverage is rather low (i.e., about only 7 km^2 between 29° and 32°S, Souvignet, Oyarzun, Verbist, Gaese, & Heinrich, 2012). Indeed, as shown by Strauch, Oyarzún, Fiebig-Wittmaack, González, and Weise (2006), meteoric water (precipitation, mainly as snow in the upper parts of the basin) strongly controls the hydrologic behavior of the watershed. As the authors state, downstream from Las Rojas (which is in turn downstream the Puclaro reservoir), "the Elqui river water maintains its ´high mountain signature´ which is due to its fast discharge from the mountain region" a behavior that is observed, with some rather minor variations, during the whole year. As a consequence of the dominant snow-driven regime, river flow attains peak discharges in late spring and early summer (October to Jaunuary), declining to low flow in the autumn (Figure 2).

A simple geological characterization of the basin shows the presence of intermediate granodioritic, calc-alkaline batholitic, and stocks intrusions in north–south trending volcanic and clastic andesitic series with minor carbonate rich-pelitic intercalations (Oyarzún, Maturana, Paulo, & Pasieczna, 2003). Groundwater resources are confined to the narrow floodplain area of alluvial sediments and to fractured rock massifs. Therefore, "groundwater plays here a minor role in comparison to that of both the northernmost and southernmost regions of Chile (Oyarzún and Oyarzún (2011)," where N–S elongated sedimentary basins are important water reservoirs with a major impact on surface hydrological processes. A preliminary estimate by Strauch et al. (2006), based on chloride and isotope mass balances, determined that groundwater contribution to the Elqui River at Gualliguaica (near the Puclaro dam) may fluctuate between 11 and 17%. Also, it is important to mention that major ion composition for surface water and groundwater is rather similar, whereas in terms of trace elements, groundwater tends to exhibit a strong depletion, especially in Fe, Cu, and As (Oyarzún et al., 2013).

The Elqui basin hosts a large number of Cu, Au, Ag, and Mn deposits. One mining district in particular is El Indio, which includes epithermal gold-enargitic rich veins, in the Andean zone close to the Argentinian border (Jannas, Bowers, Petersen, & Beane, 1999). El Indio is part of a large N–S belt of related hydrothermally altered zones, and contributes a major part of the sulphophile metals, As, and SO_4 to the

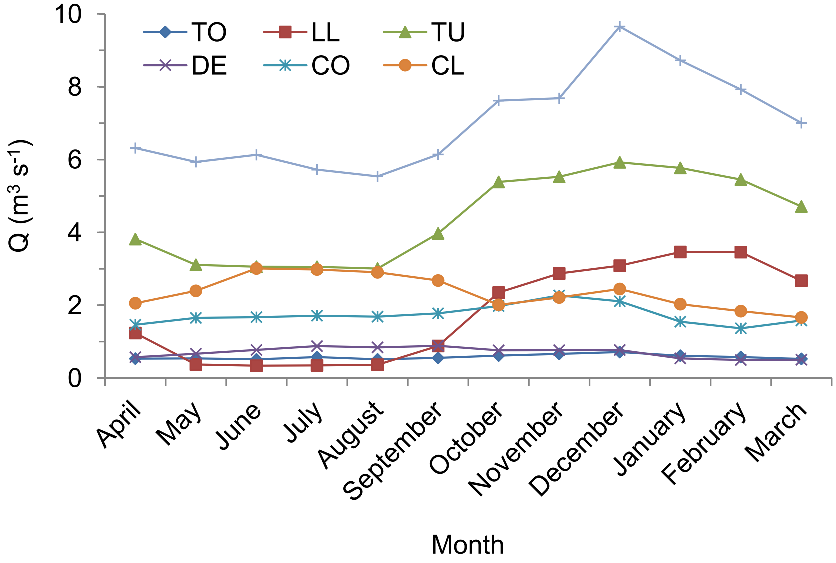

FIGURE 2 Long-term monthly median (Pexc = 50%) discharge distribution for the main rivers in the Elqui basin (data from DGA and CADE-IDEPE, 2004). TO: Toro River; LL: La Laguna River; TU: Turbio River; DE: Derecho Creek; CO: Cochiguaz River; CL: Claro River

drainage. There are several additional (and natural) factors that enhance the role of the El Indio district as a major pollution source, besides its geographical and topographical location (Oyarzun et al., 2006). They include water availability provided by snow melt, its sulfide-rich mineralogy, the existence of advanced argillic alteration zones, the occurrence of acid drainage generation, and the fact that the host rocks are highly fractured (Oyarzún et al., 2013). For a detailed description of the main contaminant sources and geochemical processes, the reader is referred to Oyarzun et al. (2004), Oyarzun et al. (2006), and Oyarzún et al. (2013).

The district has not been industrially exploited since the early 2000s, and thorough closure plan of the El Indio mining operations was implemented. This plan mainly included a settling lagoon that was built in the Malo River streambed (in the zone draining the main mineralized area), in order to especially deplete water As content. Likewise, and given the small capacity of this man-made lagoon, the Pastos Largos tailing deposit was "reconditioned" in order to behave as an As-rich sediment trap. However, despite these measures, the plan does not completely prevent the Cu-enriched acid drainage generation (Espejo et al., 2012; Galleguillos et al., 2008; Ribeiro et al., 2014).

Finally, it is important to mention that there are two water reservoirs in the basin, La Laguna (40 million m^3, Mm^3) in the Andes mountains, and Puclaro (200 Mm^3), some 50 km from its coastal end, that allow the development of an important agricultural activity in spite of the arid to semi-arid conditions of the region. This economic activity could be potentially impaired by existing natural lithological conditions or mining activities developed in upper Elqui, effects that may be enhanced by change in climate and hydrological conditions.

3 | DATA SOURCES AND ANALYSIS

3.1 | General background

As stated by Whitehead et al. (2009), "a review of surface water quality cannot be undertaken without considering changes in hydrological regime." Thus, the current study considers at first, an analysis of the temporal evolution of temperatures, precipitation and flow, along with information on water quality based on five parameters: pH, SO_4, Fe, Cu, and As. These water quality parameters were chosen in consideration of the available mineralogical and geochemical data for the Elqui basin, based on their theoretically different behavior in response to physicochemical and hydrological conditions (Guevara, Oyarzún, & Maturana, 2006; Van Vliet & Zwolsman, 2008), and their overall relevance in environmental issues associated with Andean mining activities. The metallurgical history of El Indio District (during its active exploitation) was also taken in account in this selection.

For data processing purposes, three "zones" were first defined for the study area based on information from previous studies (e.g., Espejo et al., 2012; Oyarzun et al., 2006; Oyarzún et al., 2003, 2013). These zones were named as "Zone of Alteration" (ZA), "Zone of Dilution" (ZD), and "Zone de Mixture" (ZM). The ZA is associated with the El Indio mining district, which is influenced by the hydrothermal and supergene zone of alteration, and by the mining activity conducted in the zone, resulting in acidic waters with a pH of 4 approximately (Oyarzun et al., 2006; Oyarzún et al., 2013). It includes the Malo River, Toro River, and Vacas Heladas River (E1, E2, E3, E4, E5, and E6 stations). On the other side, the ZD exhibits little or no natural factors or anthropogenic intervention affecting water quality. Previous studies have highlighted the role of the tributaries of this zone improving the water quality of the drainage system, due to their natural low load of heavy metals and alkaline pH (Espejo et al., 2012; Oyarzun et al., 2006; Oyarzún et al., 2013). This zone includes La Laguna, Ingaguaz, Estero Derecho, and Claro Rivers (E7, E9, E12, and E13 stations). Lastly, the ZM is that receiving the discharge from both the ZA and ZD areas. It includes the Turbio River and the Elqui River (E8, E10, E11, and E14 stations).

Historical information of meteorological variables, as well as surface discharge and water quality, was obtained from official records held by the Chilean Water Authority (DGA). The sampling procedure begins with the intake of unfiltered water in 0.2-L plastic bottles. The sample for Fe, Cu, and As analysis is preserved with HNO_3 (0.5 ml). Bottles are sent to the Environmental Laboratory of DGA at Santiago.

SO_4 is analyzed after filtering (0.45 μm). For Fe, Cu, and As, the sample is digested (1 ml of HNO_3 per 50 ml of sample; 150°C; 30 min), and analysis is done afterwards. Therefore, Fe, Cu, and As contents correspond to total concentrations. Analytical methods are based on Standard Methods for Examination of Water and Wastewater (Rice, Baird, Eaton, & Clesceri, 2012). SO_4 is analyzed by the turbidimetric method, with a detection limit of 2 mg/L, whereas As, Cu, and Fe are analyzed by atomic absorption, with detection limits of 0.001, 0.02, and 0.02 mg/L, respectively.

Table 1 shows the stations and the extension of the available records, while their spatial location is shown in Figure 1. For water quality sampling, the record exhibits a rather variable time frequency, but in general, they were carried out monthly or bimonthly, previous to and following 2004, respectively. Details associated with chemical analyses conducted by the DGA are described in Oyarzun et al. (2006) and Parra et al. (2011). For trend analysis (described below), records of parameters having concentrations less than the detection limit (i.e., censored values) were replaced by that limit. Thus, an annual average was calculated with the available information, which was then used for the analysis of the trends.

Given that the water source in the lower part of the zone of study (i.e., in the nearby and downstream E10 and E13) is used for agricultural activity as well as for drinking purposes, the results obtained were compared with Chilean standards, that is, NCh 1333 for irrigation and NCh 409 for potable water. The NCh 409 presents, for As and Cu, similar maximum allowed concentrations than those adopted by the World Health Organization (WHO, 2011), whereas the latter do not consider thresholds for Fe and SO_4, unlike the Chilean regulation.

3.2 | Trend analysis

To study the temporal evolution (annual average) of the parameters analyzed, the non-parametric rank-based Mann–Kendall (MK) test (Kendall, 1975; Mann, 1945) was chosen due to its suitability for data, which may not be linear nor follow a normal distribution as it is common for heavy metals (Todd et al., 2012). In addition, because the MK test is based on sign differences rather than values, it is robust regarding the effect of extreme values and outliers, and performs properly even with missing values (Helsel & Hirsch, 2002). Finally, several works have shown the usefulness of the MK test for detecting general trends in hydrological studies (e.g., Arumí et al., 2014; Weihong, Yaning, Xingming, Xiang, & Yapeng, 2007), and in the Elqui River basin in particular (e.g., Ribeiro et al., 2014; Souvignet et al., 2012).

The MK test is based on the difference between successive years of data ($x_i - x_j$) for a given period (i and j denoting the successive years). A test statistic (S) is estimated as the summation of signs (−1; 0; +1) as:

$$S = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} sign\left(x_i - x_j\right) \tag{1}$$

A Z value is then computed to estimate the significance level of the trend, which will increase with the number of identical successive signs. In this work, an $\alpha = 0.05$ (or lower) was considered for statistical significance (Mast, 2013). As serial correlation may affect the ability of the MK test to assess the significance of the detected trends (Yue & Wang, 2004), its presence was tested. When detected, a pre-whitening approach was followed before the MK procedure was applied (Arumí et al., 2014; Yue & Wang, 2004).

TABLE 1 Identification of meteorological, flow and water quality stations and extension of records considered for this study

Type	ID	Name	Altitude (masl)	Record period[3,4]
Meteorological				
	EL	La Laguna	3,160	1970–2012/1976–2012
	ET	Turbio River	2,150	1990–2012/1990–2012
	EH	Huanta	1,240	1989–2012/
	ER[1]	Rivadavia	820	1970–2012/1974–2012
	EO	La Ortiga	1,560	1979–2012/1979–2012
Flow and water quality				
	E1	Dren G	3,608	1995–2012/1986–2012
	E2	Malo River after El Indio	3,245	1981–2012/1986–2012
	E3	Baños del Toro	3,200	1981–2012/
	E4	Malo River before Vacas Heladas River	2,558	1995–2012/1986–2012
	E5	Vacas Heladas River before Malo River	2,551	1995–2012/1986–2012
	E6	Toro River before La Laguna River	2,091	1981–2012/1985–2012
	E7	La Laguna River before Toro River	1,160	1981–2012/1986–2012
	E8	Turbio River after Toro and La Laguna confluence	2,060	1981–2012/1986–2012
	E9	Incaguaz River before Turbio River	1,674	1981–2012/1989–2012
	E10[2]	Turbio River in Huanta	1,195	1986–2012/
	E11	Turbio River in Varillar	860	1981–2012/1970–2012
	E12	Estero Derecho in Alcohuaz	1,645	1984–2012/1983–2012
	E13	Claro River in Rivadavia	820	1981–2012/1970–2012
	E14	Elqui River in Algarrobal	760	1981–2012/1970–2012

[1]*Note*. Only precipitation (no temperature record).

[2]Only water quality stations (no systemic records of flow).

[3]For meteorological stations, the reported record periods are for precipitation and temperature, respectively.

[4]For flow and water quality stations, reported record periods are for water quality and discharge, respectively.

For the cases where a trend was detected, the slope was estimated using the non-parametric Sen's method (Sen, 1968), which calculates the median of all possible pairwise slopes, and is referred to hereafter as Sen's slopes (Helsel & Hirsch, 2002). A positive value of Sen's slope indicates an upward trend (i.e., increasing with time), whereas a negative value indicates a downward trend (i.e., decreasing with time). The execution of these steps (MK and Sen's method) was carried out using the MAKESENS macros provided by the Finnish Meteorological Institute (http://en.ilmatieteenlaitos.fi/makesens), while the auto-correlation analysis was performed with Minitab 15 software. It is important to note that the statistical analysis of the trends (MK test) was only conducted for those series having a minimum of 30 years of data.

Finally, a complementary Spearman correlation analysis between the water quality parameters (pH, SO4, Cu, Fe, and As) was carried out using SigmaPlot 12 software.

3.3 | Discharge versus water quality relationship

The trend analysis was complemented with a regression analysis between the flow (Q) and the concentration of each water quality parameter (SO_4, As, Cu, and Fe). The rationale behind this is that in order to estimate future trends in water quality, it is imperative, along with the characterization of past trends, to assess the effect that higher or lower flows could have on the concentrations of the different parameters under study.

From the existing 14 monitoring stations, two of them (Baños del Toro and Turbio River in Huanta) were left out of this analysis for not having systematic records of discharge. Additionally, records with censored values for the water quality parameters under study were excluded from this analysis. Lastly, from all the data available, only those containing the measure of the flow and a concurring (i.e., with a time lag of no more than 3 days) water quality sample were considered for the analysis. In any case, over 91% of the records finally considered corresponded to measurements of Q and water quality samples obtained the same day.

For each station and parameter (12*4 = 48 combinations) the goodness of fit of discharge (m^3/s) versus concentration (mg/L) was evaluated for six models: (1) linear ($y = ax + b$), (2) simple logarithmic ($\log y = ax + b$), (3) double logarithmic ($\log y = a \log x + b$), (4) second degree polynomial ($y = ax^2 + bx + c$), (5) power ($y = ax^b$), and exponential (6) ($y = ae^{bx}$) (Malan, Bath, Day, & Joubert, 2003). In order to minimize the effect of extreme values, linear regression model fitting was done by the Iteratively Reweighted Least Squares procedure, with initial estimates of β and σ given by the LS estimate and the rescaled Median Aditive Deviation, respectively (Lourenco, Piers, & Kirst, 2011).

The goodness of fit of each model was analyzed using three criteria: Akaike Information Criteria, Bayesian Information Criteria, and the root mean square error (Akaike, 1973; Kabo-bah, Yuebo, & Yajing, 2012; Schwarz, 1978). The best goodness of fit model was finally determined as that selected by at least two of the three criteria previously described. Once the best model of fit was chosen, its statistical significance was calculated using the *p*-value, keeping in mind that in the case of the nonlinear models 4, 5, and 6, the standard error as well as the covariance matrix of the coefficients is only an estimation (Graybill & Iyer, 1994). Similar to the trend analysis, a significance level of 5% was considered for results interpretation purposes. Furthermore, the type of the flow-concentration relationship (positive or negative) was determined based on the sign (+ or −) of the coefficient that accompanies the independent variable (flow) in each of the regression models analyzed, being in the case of model 4 the coefficient that accompanies the quadratic component. The analyses described in this section were conducted in R using the lm procedure from the STATS package (R Core Team, 2014) for the linear models and the nlsLM procedure from the MINPACK.LM package (Elzhov, Mullen, Spiess, & Bolker, 2013) for the nonlinear models.

4 | RESULTS AND DISCUSSION

4.1 | Trend analysis

4.1.1 | Meteorological variables

The time-series plots for precipitation and temperature are presented in Figure 3. Given the self-imposed requirement regarding data availability, that is, to have at least 30 years in order to perform trend analysis, the latter was only carried out for the stations at La Laguna (EL), La Ortiga (EO), and Rivadavia (ER), without detecting statistically significant trends for them. These results are in accordance with those described by Souvignet et al. (2012). Nonetheless, it is fair to say that at least a slight to moderate decrease in precipitation is apparent for the last 30 to 40 years. Actually, when the first 15 years of each recorded period are compared with the last 15 years for La Laguna (EL), La Ortiga (EO), and Rivadavia (ER) stations (the three with longer records), a decrease of about 30% is detected in the annual precipitation. This behaviour was not detected for temperature (except in ER).

4.1.2 | Discharge

Flow time series (Figure 4) were only statistically evaluated at stations E11 to E14, that have information of an appropriate extension (i.e., at least 30 years). Although only E12 (Estero Derecho in Alcohuaz) presents a statistically significant decreasing trend (Table 2), independent from the extension of the series, decreasing flow patterns are observed for the entire study zone. Considering the stations with the most extended records, such behaviour has been particularly important since the mid-80s.

4.1.3 | Water quality

Figures 5, 6, and 7 present the time series data for the different parameters (pH, SO_4, Fe, Cu, and As) and stations analysed (for the sake of comparison, all the scatterplots are drawn with the same scale), whereas Table 3 summarizes the trend analysis results.

Regarding pH, and with the exception of E3 and to some extent E5 (despite the short record period for the latter), the ZA is generally characterized by the presence of acid waters (Figure 5), a direct consequence of the ARD generation at this highly mineralized area. It was possible to detect two statistically significant trends, both decreasing ones, at E2 and E6. However, it is important to note that both stations, as well as E1 and E4, exhibit an increasing pattern from around 2005. On the other hand, rivers in both the ZD and the ZM (Figures 6 and 7,

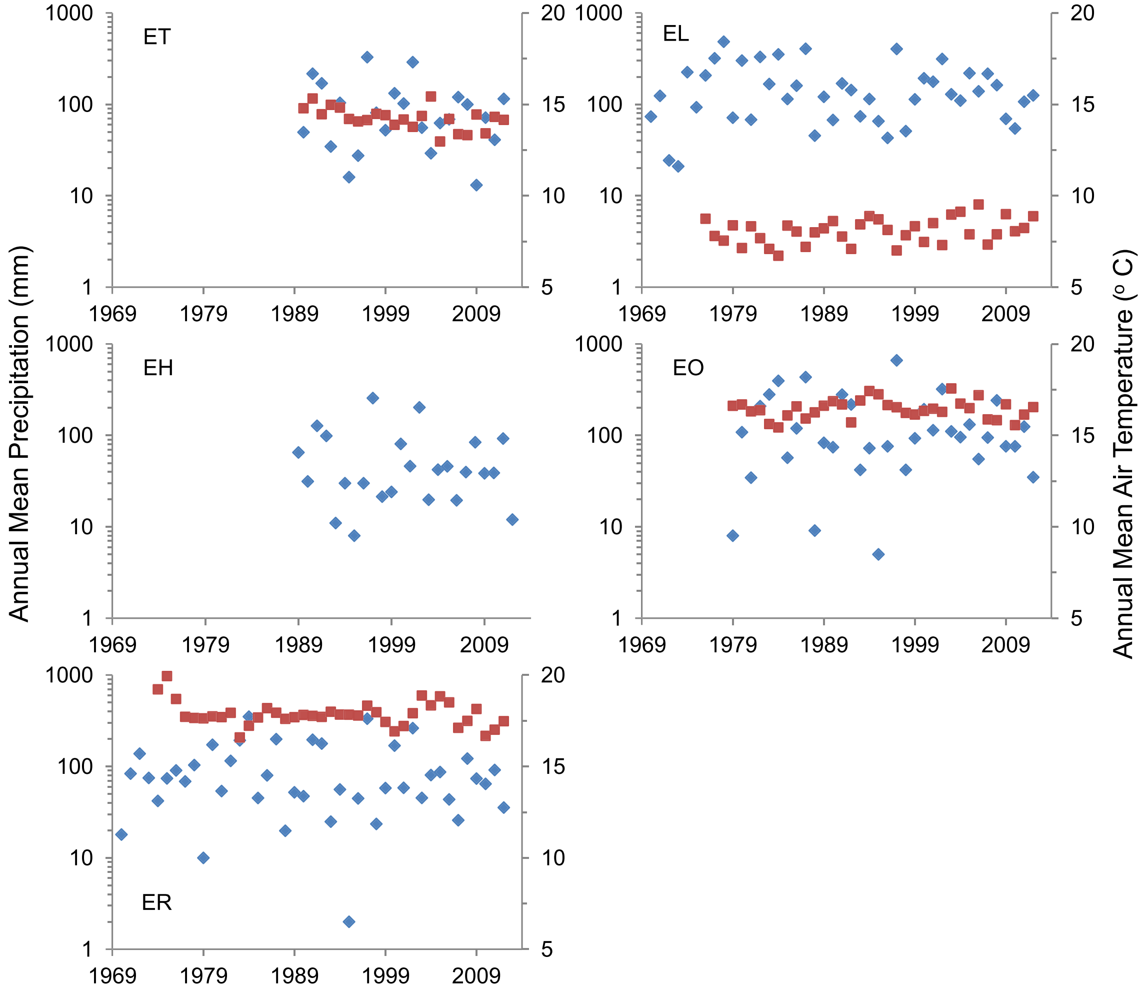

FIGURE 3 Time series of total annual precipitation (mm) and annual mean air temperature (°C) for La Laguna station (EL), Turbio station (ET), Huanta station (EH), La Ortiga station (EO), and Rivadavia station (ER). Blue squares correspond to precipitation while red squares represent temperature

respectively) present moderately alkaline pH. Along with some oscillating behaviour on the annual pH values (e.g., E8 in the ZM and E9 in the ZD), there are no major long-term changes in the pH of the waters, as only three stations (from both ZD and ZM) exhibit statistically significant increasing trends but with rather low sen's slopes values (Table 2). Finally, pH values at ZD and ZM comply with both the NCh1333 and NCh409 regulations (5.5–9.0 for the former and 6.5–8.5 for the latter).

In the case of SO_4, the time series plots show that for ZA (Figure 5), the concentrations are particularly high, largely exceeding the thresholds established by the NCh 409 and 1333 standards (500 and 250 mg/L, respectively), which agree with the results obtained by Oyarzun et al. (2006) and Espejo et al. (2012). At least four of the six stations show an increasing pattern after ca. 1990, although this is only verified in terms of statistical significance for E6 (Toro River before La Laguna River). Rivers in the ZD, that is, La Laguna, Incaguaz, and Claro (Figure 6) exhibit concentrations that are considerably lower than those of ZA. However, a generally increasing pattern is also appreciated, which is statistically significant at three of the four monitoring stations in the zone (E7, E9, and E13). All of this results in that sulphate concentrations for ZM (Figure 7) exhibit increasing patterns as well, which are statistically significant in three of the four stations within that zone (E8, E11, and E14), with values nearing or exceeding the irrigation standard, especially from the year 2000.

In the case of Fe, it is also the ZA where the greatest concentrations are found (Figure 5), largely exceeding the Chilean regulation thresholds (5 and 0.3 mg/L for NCh1333 and NCh409, respectively). Furthermore, the lowest values are seen in the ZD (Figure 6). However, while concentrations in ZD are comparatively lower than those in ZA, the potable water standard (0.3 mg/L) is exceeded in most years. Lastly, the ZM (Figure 7) exhibits intermediate concentrations, generally complying with the requirements established in the irrigation standard (5 mg/L), except in E8, although exceeding the potable water standard. In terms of the temporal evolution of the concentrations, they do not present a behaviour that allows the determination of statistically significant trend, either increasing or decreasing ones, in any of the zones.

For Cu in the ZA (Figure 5), along with extremely high levels (similar to those described for the other parameters), two increasing trends are identified for E2 (Malo River downstream El Indio) and E6 (Toro River before La Laguna River). However, a detailed analysis shows that in the overall, the concentrations have started to decline since 2002 in this zone, which coincides with the cease in mining activities at the El Indio mine and its closure plan. For the case of ZD (Figure 6), in spite of

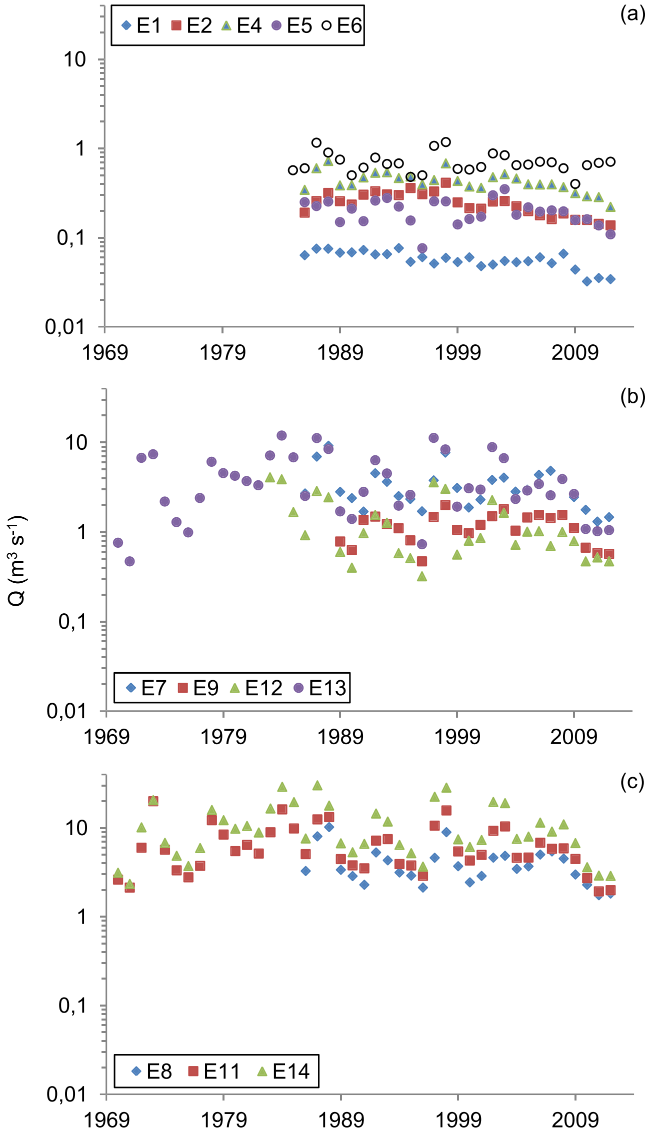

FIGURE 4 Time series plots of average annual discharge (Q, m^3/s). (a) ZA stations (E1, E2, E4, E5, and E6); (b) ZD stations (E7, E9, E12, and E13); and (c) ZM stations (E8, E11, and E14)

the low values, it is observed an increasing pattern at E12 and E13 stations, although the time series are not statistically significant. Finally, three stations (E8, E11, and E14) exhibit statistically significant increasing trends in ZM (Figure 7, Table 2). In addition, although the drinking water threshold (2 mg/L) is not generally exceeded, Cu levels do exceed the irrigation standard (0.2 mg/L).

Arsenic presents different relationships from those described for Cu, and behaves more like Fe, which is explained by the fact that this element is adsorbed and transported by $Fe(OH)_3$ colloidal particles (Oyarzun et al., 2006). High values of As in the ZA (Figure 5) highlight (extremely elevated in the zone with thermal activity, E3 Baños del Toro), which sharply contrast with the low concentrations in rivers in the ZD (Figure 6), particularly Incaguaz and Claro (stations E9, E12 and E13). For the latter zone, statistically significant decreasing trends were detected in E9 and E13. Lastly, ZM (Figure 7) presents intermediate values that in overall exceed the NCh 409 but not the NCh 1333 (0.01 and 0.1 mg/L, respectively). In this zone, it was possible to detect two statistically significant decreasing trends, for E8 and E11, but in general, the plots exhibit decreasing concentrations from the early 90s.

Finally, the results of the correlation analysis are shown in Table 3. It is of interest to note that most of the statistically significant correlations detected are between Fe-As, Fe-Cu, and SO_4-Cu (in all the cases all of them were positive ones). The Fe-As correlation is easy to explain given the absorption of As by $Fe(OH)_3$ colloidal particles. Fe and Cu contents are both linked to the ARD process acting at the El Indio district and related hydrothermal and supergene alteration zones. SO_4 and Cu are associated by their common sources in enargite (Cu_3AsS_4). The fact that SO_4 and As do not present a consistent correlation could be explained by the different sources of both substances. In fact, although both are present in enargite, SO_4 is a common component of any hydrothermal solution and a product of the weathering of any sulphide mineral. In exchange, As is linked to more specific hydrothermal sources. Regarding pH, it was only relevant for As (mostly negative correlations) and SO_4 for the ZA (also negative correlations).

4.2 | Discharge-water quality relationships

Table 4 shows the results of the model fit procedure between flow and water quality.

For SO_4, there were only logarithmic (simple or double) relationships between surface flow and concentration, which were negative

TABLE 2 Trend analysis results for discharge and water quality parameters. Upward and downward arrows respectively denote increasing or decreasing statistically significant (5%) trend (and in those cases the Sen slope is given), empty cells correspond to no trend detected, whereas "nd" denote short time series, (n < 30) so no statistical analysis was performed

Zone	Station	Q	pH	SO4	Fe	Cu	As
ZA	E1	nd	nd	nd	nd	nd	nd
	E2	nd	↓ (less than −0.1)	nd		↑ (0.9)	↑ (<0.1)
	E3	nd		nd			
	E4	nd	nd	nd	nd	nd	nd
	E5	nd	nd	nd	nd	nd	nd
	E6	nd	↓ (less than −0.1)	↑ (10.6)		↑ (0.5)	↓ (less than −0.1)
ZD	E7	nd	↑ (<0.1)	↑ (1.1)			
	E9	nd		↑ (1.1)			↓ (less than −0.1)
	E12	↓ (less than −0.1)		nd			
	E13		↑ (<0.1)	↑ (1.0)			↓ (less than −0.1)
ZM	E8	nd		↑ (4.5)		↑ (<0.1)	↓ (less than −0.1)
	E10	nd	nd	nd	nd	nd	nd
	E11			↑ (2.8)		↑ (<0.1)	↓ (less than −0.1)
	E14		↑ (<0.1)	↑ (2.3)		↑ (<0.1)	

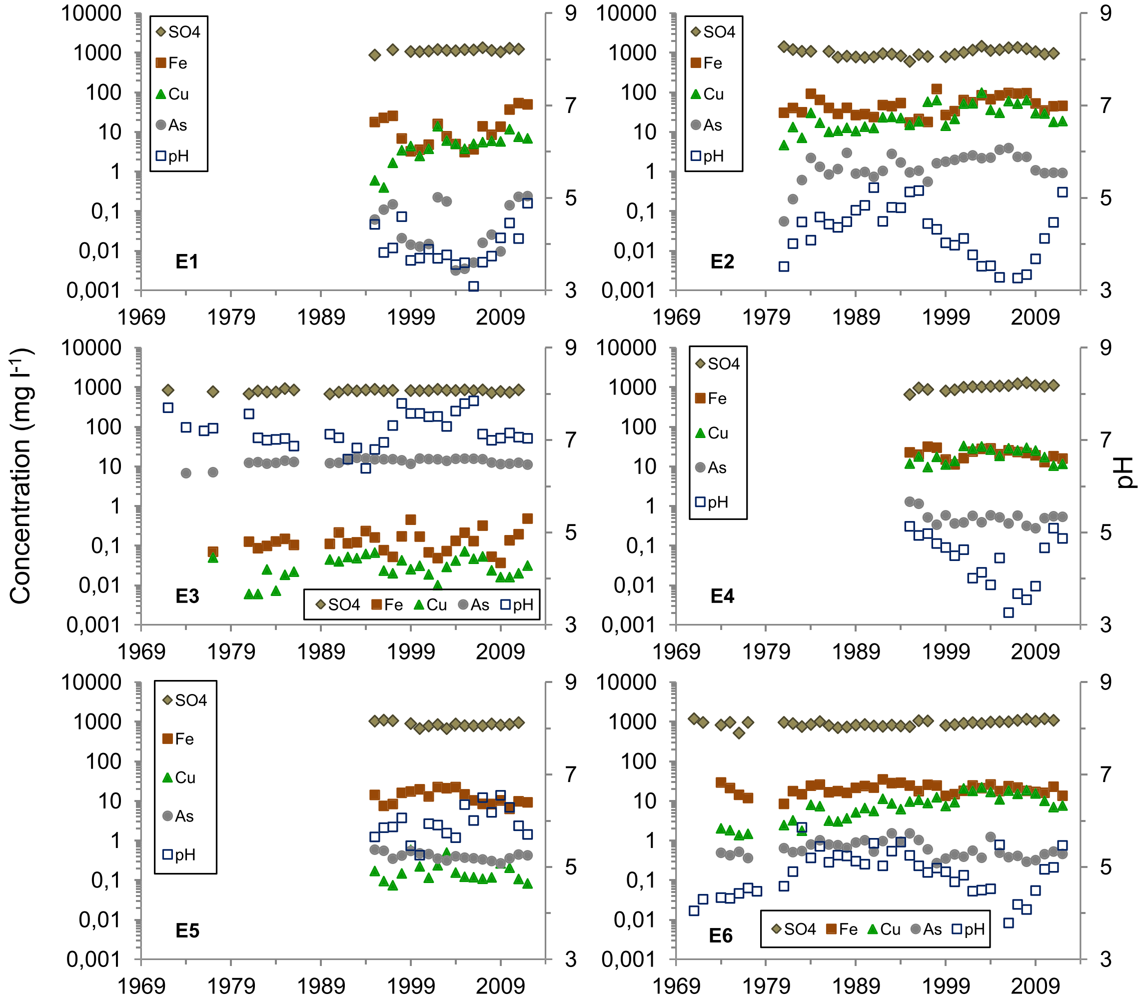

FIGURE 5 Time series plots of average annual pH, and SO_4, Fe, Cu, and As concentrations (mg/L) for the ZA stations (E1, E2, E4, E5, and E6)

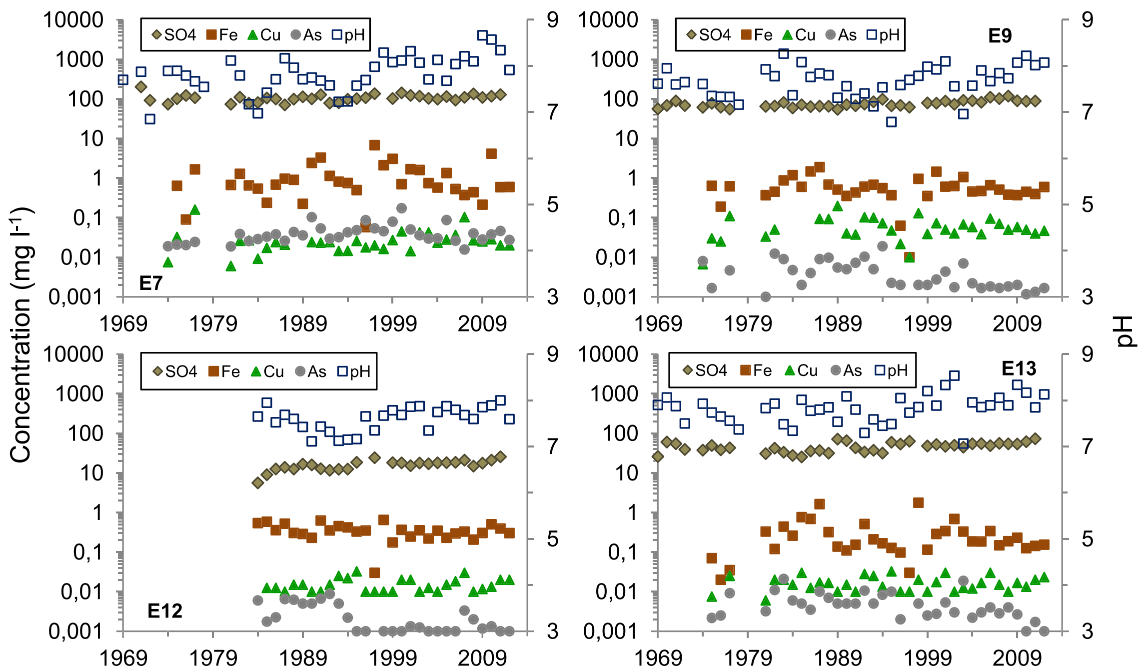

FIGURE 6 Time series plots of average annual pH, and SO_4, Fe, Cu, and As concentrations (mg/L) for the ZD stations (E7, E9, E12, and E13)

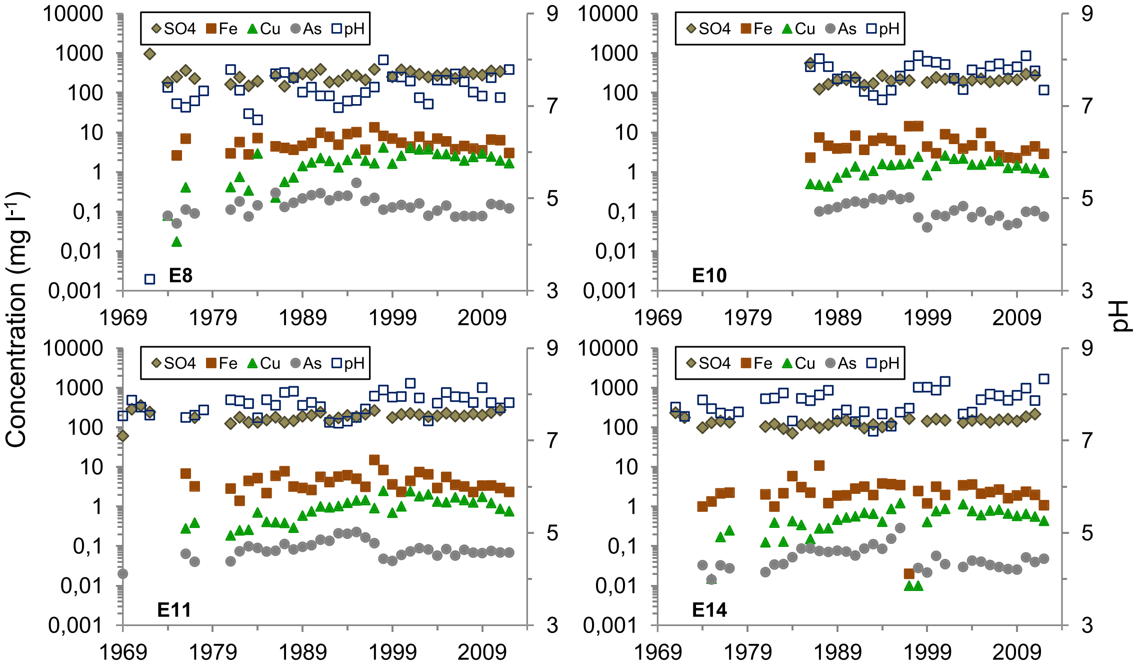

FIGURE 7 Time series plots of average annual pH, and SO_4, Fe, Cu, and As concentrations (mg/L) for the ZM stations (E8, E10, E11, and E14)

(i.e., inverse) in 10 of the 12 stations that were analyzed, all of which were statistically significant.

Fe shows a behaviour similar to that of SO_4 in terms of predominance (9 of 12 stations) of simple or double logarithmic relationships (four and five cases, respectively), being all of them statistically significant, probably a consequence of the dominance of pyrite (FeS_2) weathering as the principal source for both Fe and SO_4. Nonetheless, a difference of Fe behaviour respect to SO_4 is that for Fe, in 9 of the 12 stations a positive (i.e., direct) relationship between flow and concentration was detected (with eight of these cases being statistically significant). This positive relationship was observed for the four stations in ZD (with three of them statistically significant), and in two of the three stations in ZM, and suggests that turbulent flow associated with higher discharges favours the transport of particulate forms of Fe (e.g., FeOOH, $Fe(OH)_3$).

Unlike SO_4 and Fe, for Cu and As, a more erratic behaviour in the flow-concentration relationship is observed, with a very slight predominance (7 of 12 stations) of negative relationships for both parameters. In particular for Cu, four of these inverse relationships (i.e., 33% of all the stations considered) are statistically significant. Furthermore, differences were observed regarding the model of best fit, with double logarithmic and exponential being more frequent, with four cases each (and five of these eight relationships being statistically significant). Lastly, the behaviour among zones is equally variable. For example, three statistically significant negative relationships and two positive ones (being one of them statistically significant) were obtained in ZA. A similar behaviour was observed in the ZD, where three positive and two negative relationships were observed (only one positive relationship having statistical significance). For As, and similar to Cu, an inverse relationship at 7 of the 12 stations was observed, of which four were statistically significant. However, unlike Cu, As presented an exponential model as best fit at 8 of the 12 stations (four of these eight cases being statistically significant). In addition, four of five stations in the ZA presented a negative relationship (two of them being statistically significant), whereas in the ZD two of four stations exhibited positive (but not statistically significant) relationships.

TABLE 3 Spearman correlation analysis (5% significance level) between water quality parameters

Zone		pH-SO_4	pH-Fe	pH-Cu	pH-As	SO_4-Fe	SO_4-Cu	SO_4-As	Fe-Cu	Fe-As	Cu-As
ZA	E1		+		+		+			+	
	E2	−	−	−	−	+	+		+	+	+
	E3							+	+		+
	E4	−		−							
	E5				−				+		
	E6	−			+		+			+	
ZD	E7	+						+		+	
	E9								+	+	+
	E12				−	−		−			
	E13	+			−	−	+	−		+	+
ZM	E8					+		+	+	+	
	E10				−						
	E11						+			+	
	E14				−					+	

+ = positive correlations; − = negative correlation

TABLE 4 Best models, statistical significance and type of relationship between flow (x) and concentration of the different water quality parameters (y), for the different stations and zones considered

Zone	Station	Parameter	Best Model	*p*-value	Relationship	Parameter	Best Model	*p*-value	Relationship
ZA	E1	SO_4	f2	.440	+	Fe	f2	.016*	−
ZA	E2	SO_4	f2	.000*	−	Fe	f3	.024*	−
ZA	E4	SO_4	f2	.012*	−	Fe	f3	.000*	+
ZA	E5	SO_4	f3	.000*	−	Fe	f3	.027*	+
ZA	E6	SO_4	f2	.000*	−	Fe	f3	.000*	+
ZD	E7	SO_4	f3	.000*	−	Fe	f2	.000*	+
ZD	E9	SO_4	f3	.001*	+	Fe	f6	.084	+
ZD	E12	SO_4	f2	.000*	−	Fe	f5	.000*	+
ZD	E13	SO_4	f3	.000*	−	Fe	f6	.000*	+
ZM	E8	SO_4	f3	.000*	−	Fe	f3	.000*	−
ZM	E11	SO_4	f3	.000*	−	Fe	f2	.000*	+
ZM	E14	SO_4	f3	.000*	−	Fe	f2	.000*	+
ZA	E1	Cu	f2	.028*	−	As	f6	.010*	−
ZA	E2	Cu	f3	.002*	−	As	f3	.060	−
ZA	E4	Cu	f3	.102	+	As	f6	.245	+
ZA	E5	Cu	f6	.000*	−	As	f6	.000*	−
ZA	E6	Cu	f3	.013*	+	As	f5	.690	−
ZD	E7	Cu	f5	.064	+	As	f6	.000*	−
ZD	E9	Cu	f6	.000*	+	As	f6	.124	+
ZD	E12	Cu	f5	.473	−	As	f6	.963	−
ZD	E13	Cu	f6	.083	+	As	f6	.067	+
ZM	E8	Cu	f3	.000*	−	As	f6	.000*	−
ZM	E11	Cu	f6	.378	−	As	f5	.000*	+
ZM	E14	Cu	f4	.052	−	As	f5	.357	+

Note. f1: linear ($y = ax + b$); f2: simple logarithmic ($\log y = ax + b$); f3: double logarithmic ($\log y = a \log X + b$); f4: second degree ($y = ax^2 + bx + c$); f5: power ($y = ax^b$); f6: exponential ($y = ae^{bx}$); +: positive (direct) relationship; −: negative (inverse) relationship

Statistical significance (5%) is denoted by "*"

This difference in behaviour for the parameters considered is related to their different properties determining their presence in the water column, either in the dissolved phase or adsorbed onto suspended solids in the water column. A related analysis is presented by van Vliet and Zwolsman (2008), who studied the effect of summer droughts on the water quality in the Meuse River basin in Europe. These authors found that for metals with low partition coefficients (Kp, L/g), which are predominantly present in the dissolved phase in the water column, such as Se, Ba, and Ni (Kp between 0.59 and 8), it was normal to find a negative relationship between flow and concentration. In contrast, for elements with a high Kp (higher than 130), that is, with greater proportions adsorbed to solids in suspension, such as Cd, Hg, Cr, and Pb, they found a positive relationship of the exponential type between discharge and concentrations. Lastly, for elements with an intermediate Kp such as As, Cu, and Zn (Kp between 10 and 110), it was not possible for the authors to establish a clear relationship. In this aspect, the aforementioned results are in agreement with the findings of the current study for As and Cu (common elements for comparison) having similar behaviours.

These findings are important as they highlight the fact that potential effects of future modifications in hydrological processes due to flow variations, as a consequence of changes in climate, do not necessarily determine a single type of response (i.e., either beneficial or detrimental) in terms of water quality in a given area.

4.3 | Climate variability/climate change effect on water quality

The third and last analysis of this work refers to the qualitative estimation of potential effects of future climate modifications on the water quality based on the parameters considered in this study for the upper Elqui basin. The effect of climate change on water quality should be considered under a wider framework, related to changes on hydrological regimes and how these could translate into water quality variations.

It is important to acknowledge that this section is the most complex and challenging of the current contribution, given several factors:

1. As shown previously, the water quality parameters analyzed do not exhibit a single behaviour (i.e., either only positive or negative relations) with respect to changes in surface flow. Thus, a given expected change in future hydrological conditions should likely translate into different results in terms of water quality for the different parameters considered.
2. The existing data used in this study covers a rather limited time period, something that unfortunately is common in developing countries and in mountain basins. This adds difficulty when inferring if the identified past patterns and trends will persist in the

future had the data been more extensive, as it is known that key hydrological aspects of Andean watershed (e.g., rivers streamflow) exhibit inter-decadal regime shifts as a consequences of different phases of El Niño-Southern Oscillation and specially Pacific Decadal Oscillation (Núñez et al., 2013).

3. It is also important to consider that climate change model predictions and their downscaling at the basin scale still present levels of considerable uncertainty (Glavan et al., 2015; Kundzewicz et al., 2008). This is a consequence of the models of global circulation themselves, and the use of downscaling techniques for zones with complex geomorphological configurations (i.e., abrupt changes in altitude and irregular slope) as occurs in north-central Chile (Souvignet et al., 2010).
4. In the long term, likely changes in the seasonal patterns of both precipitation and temperature, as a consequence of climate change, could affect the hydrological behaviour (and therefore, water quality) of mountain basins in different ways (Vuille et al., 2008). This is due to the fact that key hydrological processes at each watershed depends on factors such as local geomorphology as well as on the percentage of area covered by snow and glaciers (whose contribution to the surface discharge becomes more relevant during years of low precipitation). Thus, along with the overall importance of the climate and particularly the snow fall (accumulation and dynamic of snow melt) over the hydrology in zones like the upper Elqui valley, local characteristics such as valley orientation, hill slope exposures, percentage of area covered by glaciers, abrupt elevation changes, and catchment hypsometry should also be considered when trying to forecast their hydrological response to climate modifications (Souvignet et al., 2010; Vuille et al., 2008). As shown in Cornwell, Molotch, and McPhee (2016), even nearby watersheds exhibit differences in terms of snow water equivalent (associated to the snow accumulation) for the same altitudinal belt (i.e., 3,000–5,000 masl). Regarding altitude distribution, Figure 8 shows the hypsometric relationships of several basins in the area of study. It is of interest to acknowledge the important differences observed. Indeed, while in the sub-basins of the Malo and Laguna Rivers (part of the ZA and ZD, respectively) 50% of the surface is found above 4,000 m, this altitude is reduced, for the same area percentage, to 3,000 m for the Incaguaz and Claro sub-basins (both found in the ZD). Considering that snowpack will mostly accumulate and therefore will have a higher relevance in terms of hydrological processes (river discharge) at elevations above 4,000 masl (Sproles, Kerr, Orrego, & López, 2016), it turns out evident that the effects of climate change on local hydrology, and therefore water quality, should be different in the considered sub-basins because of the described factors.
5. Given the limited existing information, the role of subsurface storage potentially offsetting the effect of changes in snow accumulation over river discharges was not addressed in the current work. Although this hydrological component could be of some importance in alpine systems (Markovich, Maxwell, & Fogg, 2016; Tague, 2009), our previous studies for the Elqui basin (e.g., Oyarzún et al., 2013; Strauch et al., 2006) allowed us to consider it of minor relevance in terms of its contribution to surface flow.

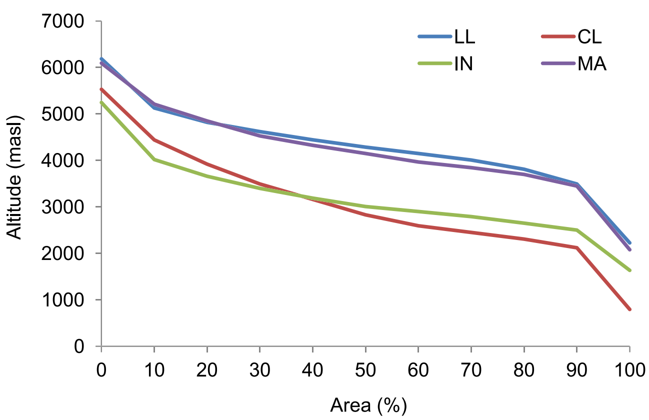

FIGURE 8 Hypsometric curves for selected rivers. LL: La Laguna River; CL: Claro River, IN: Incaguaz River; MA: Malo River

In spite of all the complexities discussed, it is important to attempt the analysis in terms of the effect of climate change on local hydrological processes and from that, on water quality. In fact, one of the 25 proposed improvements to the Chilean environmental regulatory framework recently made by a governmental advisory commission refers to the "consideration of climate change in the Environmental Impact Assessment System" (MMA, 2016). Thus, it becomes clear that despite the complexity (and sometimes uncertainty) the process of climate change present, as it effects on local hydrological processes, this issue will likely be an integral part of future hydrological and specially hydro-environmental studies related with water quality, both in Chile as well as in other countries of the region.

The existing climate change studies, both on a global level (e.g., Kundzewicz et al., 2008) as well as for central and north-central Chile (e.g., De Maria et al., 2013; Souvignet et al., 2010; Vicuña, Garreaud, & McPhee, 2011), generally point towards warmer and drier conditions for the future, which would translate into changes in the quantity, timing, and variability of water resources availability (Bartnett et al., 2005). Precipitation in the area of study falls mainly during winter, and hence, snow that can accumulate during this period as well as glaciers are the main natural water reservoirs. Thus, a significant increase in winter and summer temperatures would reduce snow cover and accelerate the snow melt, and hence, peaks in flow (late spring or early summer) would develop earlier, decreasing river flow during the rest of the season and over the long run. In fact, De Maria et al. (2013) forecast, for the Mataquito basin (an alpine watershed in Central Chile), that the Center of Timing, that is, "the day when half the annual (water year) flow volume has passed a given point," would happen, for the 2020–2049 period, 12 days earlier on average than the historical 1960–1989 period as consequence of climate change. A change from snow to rain precipitation as well as in flow behaviour (timing, peak, and specially the occurrence of transient "flash flood" events) could foster erosion processes and certainly may have an instantaneous effect (i.e., associated to the days of a given event) on water quality, given a likely higher load of suspended solids (Nordstrom, 2009; Pizarro, Vergara, Morales, Rodríguez, & Vila, 2014). However, and regarding mid to long term effects, which is the main focus of this work, and in particular for Upper Elqui valley, Souvignet et al. (2010) projected for the coming decades a negative trend in annual precipitation (−4.7% per decade, on average), which would be more pronounced in zones of greater elevations. Also important, these authors also describe a likely change in temperature patterns as well (increase of 0.14 to 0.58°C per decade), which would again occur faster in zones of higher altitudes. This should have an impact on the hydrological behaviour of the area, considering that changes in flow within these mountain zones are more sensitive to changes in temperature than to changes in precipitation (Gascoin et al., 2011; Souvignet et al., 2010).

Considering these projections and the results previously described (i.e., trend analysis and flow-concentration relationships), the following outcomes, both in terms of hydrological processes and water quality, can be inferred:

1. A process of temperature increase and precipitation decrease would determine a general decrease in surface flow, which might be of greater significance in the basins of the Malo and La Laguna Rivers (given their higher altitude and hypsometric characteristics and the consequently more important contribution from the snow/rainfall to their hydrological behaviour). Considering that the Malo River drains the mineralized zone of El Indio, this could represent a favourable situation in terms of water quality from the point of view of a decrease in the overall burden of contaminants actually transported by the river. This would especially affect those parameters whose concentrations tend to be proportional to the flow (e.g., Fe) or that are transported in part adsorbed to suspended clay minerals or ferruginous material, as is the case of As and Cu, whose concentrations tend to decrease with a lower discharge. However, at the same time, this could translate into higher concentrations of SO_4, which in any case, represents a parameter of lesser worry, both environmentally as well as in terms of public health, when compared to the other parameters analyzed in the current study.
2. Although the aforementioned situation seems, in general, beneficial, it is important to not ignore the effect a lower flow of the La Laguna River would have, given that it plays an important role in the dilution of high levels of heavy metals transported by the Toro River. Therefore, if the contaminant burden transported by the latter decreases due to a reduction in surface flow, it would also decrease the buffer capacity related with the physical (due to their flow) and chemical (due to alkaline pH) dilution processes exerted by the former.
3. Also, it is important to acknowledge that two additional rivers play a depurating role as well: the Incaguaz and Claro Rivers. The Incaguaz River presents a low flow in comparison to the other rivers considered in the study, and hence, its effective role in terms of water quality improvement is much less. With respect to the Claro River, and according to the current projections, a significant decrease in its flow due to climate change is not to be expected, at least when compared to other sub-basins located at higher altitude. However, and as it was previously shown, the E12 (Estero Derecho) station has registered an important decrease in flow since the early 80s. Although there is a second tributary in this sub-basin (Cochiguaz River) with higher discharge that explains the fact that the mentioned decrease in flow in E12 does not clearly manifest in E13 (Claro River in Rivadavia), this situation should be considered with particular attention. In fact, any industrial activity (e.g., mining) that could be developed in this area (especially in the sub-basin of the Cochiguaz River) constitutes a relevant risk factor in terms of impairing its natural depurating capacity and, therefore, should be environmentally assessed with special attention. In fact, Oyarzun et al. (2006) showed how incipient mining work (e.g., exploration stage and initial development) in La Laguna River at the end of the 90s quickly translated into an increase in levels of As, Cu, and Fe, which reinforces the idea of the vulnerability of these Rivers to potentially contaminant activities.

In summary, the Elqui River basin presents a complex situation in terms of water quality bearings of driving hydrological processes. Even if the adopted closure measures by the El Indio mine as well as climate change projections point to an overall rather favourable situation in terms of water quality (specially for Fe and eventually As and Cu), this delicate balance could be easily altered if activities that may affect both quantity and quality of the water in tributaries, such as La Laguna and in particular Claro River, are conducted. Similar situations could arise in other Andean basin located in comparable contexts (for example the Huasco basin associated to the mega Au-Cu Pascua Lama project), which should be carefully considered when assessing possible impacts of new projects, as well as when monitoring their development in these basins that are sensitive to climate change and variability.

5 | CONCLUSIONS

The following main conclusions can be drawn from this study:

1. Overall, there is a certain decoupling between the meteorological variables and the surface water flow in the area of study. With respect to the discharge, while there seems to be decreasing patterns for the historical series analyzed, only one statistically significant trend was determined (Estero Derecho in Alcohuaz station).
2. The ZA exhibits low pH and very high levels in the different water quality parameters considered (SO_4, Fe, Cu, and As). Although rivers in the ZD zone that come from the southeast have an important depurating effect on the water improving its quality, it is possible to find high levels of the analyzed elements that exceed Chilean standards even in the ZM.
3. In terms of long-term water quality, while SO_4 shows overall increasing patterns, which are statistically significant for some stations, Fe as well as Cu and As presents different and more complex behaviours.
4. There is no single flow-concentration behaviour pattern for the different water quality parameters considered. While SO_4 exhibits a negative relation, Fe tends to exhibit a positive one, and neither Cu nor As exhibit a single, easily identifiable pattern

in the entire study area. These different behaviours are the result of the chemical characteristics of the elements and compounds, particularly the greater or lesser presence of them in the dissolved or the particulate phase (in the water column). This is an important factor to consider when evaluating the possible effect of modifications to the flow (independent of the cause) on water quality.

5. Given the projections regarding climate change that mostly point towards warmer and drier conditions, as well as the characteristics of the different sub-basins in the study area, it is possible to expect a decrease trend in discharge in the long term in the upper ones, such as the Malo River sub-watershed. Considering that the current main source of acid drainage pollution for the Elqui basin is indeed in the Malo sub-basin (El Indio district), this situation seems favourable for the Elqui watershed as a whole, in terms of a lower contaminant load transported by the river (especially for Fe and to a lesser extent, As and Cu). However, this situation could be easily modified by the development of new mining or industrial activities in other rivers of the basin headwater, such as La Laguna and Claro, which currently play an important depurating role.

Lastly, it should be noted that this study addresses an issue that goes beyond the local interest and could be used as a reference to compare other transition environments containing sulphide ores or areas of hydrothermal alterations in the Andean belt, which are considered to be highly vulnerable to climate change and variability, as are areas in central-northern Chile.

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