

# Natural factors and mining activity bearings on the water quality of the Choapa basin, North Central Chile: insights on the role of mafic volcanic rocks in the buffering of the acid drainage process

Amparo Parra · Jorge Oyarzún ·  
Hugo Maturana · Nicole Kretschmer ·  
Francisco Meza · Ricardo Oyarzún

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**Abstract** This contribution analyzes water chemical data for the Choapa basin, North Central Chile, for the period 1980–2004. The parameters considered are As, Cu Fe, pH, EC,  $\text{SO}_4^{-2}$ ,  $\text{Cl}^{-1}$ , and  $\text{HCO}_3^{-1}$ , from samples taken in nine monitoring stations throughout the basin. Results show rather moderate contents of As, Cu, and Fe, with the exception of the Cuncumén River and the Aucó creek, explained by the influence of the huge porphyry copper deposit of Los Pelambres and by the presence of mining operations, respectively. When compared against results obtained in previous researches at the neighboring Elqui river basin, which host the El Indio Au–Cu–As district,

a much reduced grade of pollution is recognized for the Choapa basin. Considering the effect of acid rock drainage (ARD)-related Cu contents on the fine fraction of the sediments of both river basins, the differences recorded are even more striking. Although the Los Pelambres porphyry copper deposit, on the headwaters of the Choapa river basin, is between one and two orders of magnitude bigger than El Indio, stream water and sediments of the former exhibit significantly lower copper contents than those of the latter. A main factor which may explain these results is the smaller degree of  $\text{H}^+$ -metasomatism on the host rocks of the Los Pelambres deposit, where mafic andesitic volcanic rocks presenting propylitic hydrothermal alteration are dominant. This fact contrast with the highly altered host rocks of El Indio district, where most of them have lost their potential to neutralize ARD.

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A. Parra  
Ingeniero de Proyectos, Fundación Chile,  
Santiago, Chile

J. Oyarzún · H. Maturana · R. Oyarzún (✉)  
Departamento Ingeniería de Minas,  
Universidad de La Serena, La Serena, Chile  
e-mail: royarzun@userena.cl

N. Kretschmer · R. Oyarzún  
Centro de Estudios Avanzados en Zonas Áridas  
(CEAZA), La Serena, Chile

F. Meza  
Centro Experimental Choapa,  
Instituto de Investigaciones Agropecuarias,  
Carretera a Los Vilos, Sector Cuz-Cuz s/n,  
Paradero 4, Illapel, Chile

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## Introduction

Water availability in arid zones basins, both in terms of quantity and quality, is a key element of their sustainable development. In particular, heavy metal contamination is a relevant aspect

in arid and semiarid zones with mining activities (Dundar and Altundag 2007; Rojas and Vandecastelde 2007). This is the case of the Choapa River Basin in the southern part of the Coquimbo Region, North Central Chile, where surface drainage is the source of drinking water for more than 35,000 inhabitants and the basis for the agricultural activity on the watershed, attaining some 13,500 ha of irrigated land (INE 2005, 2007). Whereas this activity has been traditionally related with extensive crops (pastures, cereals), the recent construction of the Corrales (50 Mm<sup>3</sup>) and the El Bato (25 Mm<sup>3</sup>) reservoirs will improve the inter-annual and intra-annual water availability. Thus, it is expected that these hydraulic works will foster the agriculture of the Choapa Province, favoring the development of high valued crops such as avocado and walnut. Clearly, this effort requires irrigation water with the proper quality demanded for this purpose.

Water quality may be hampered by urban development, the agricultural activity itself (e.g., excessive use of pesticides and fertilizers), and by the effect of the present and past mining–metallurgical activity developed at a given area. Indeed, sulfides weathering and the generation of acid mine drainage has been recognized as one of the major environmental problems in sites with active and abandoned mines worldwide (Edraki et al. 2005)

For the Choapa basin, it is important to consider the existence of the Los Pelambres deposits. This is placed in the basin headwaters, and is one of the Chilean largest copper porphyry deposit, with copper (molybdenum) ore reserves over 2,125 million tons (average 0.64% Cu; 0.016% Mo), a treatment capacity rate of 175,000 tons per day and annual production (2008) of copper concentrates equivalent to 351,000 metric tons of fine copper, plus 7,700 ton of Mo concentrate (COCHILCO 2009). Also, a medium size copper deposit named Tres Valles (formerly Papomono), close to the Salamanca town in the middle course of the Choapa river, is ready to start open pit mining and heap leaching operations, in order to produce about 18,000 tons of copper cathods per year (VALE 2009). Finally, the Choapa basin presents the largest number of tailing deposits in the country (SERNAGEOMIN 1990; CONAMA

1999), several of them abandoned, which are likely sources of heavy metal pollution for surface drainage, considering its proximity to main rivers and creeks. Although the neutral to basic pH of the river waters, characteristic of arid to semi-arid basins, constraints heavy metals transport, specially copper, in the ionic form, their contents linked to the fine sediment fractions should be also considered when performing environmental assessments, as they could be later incorporated to the soils by irrigation water diverted from the rivers.

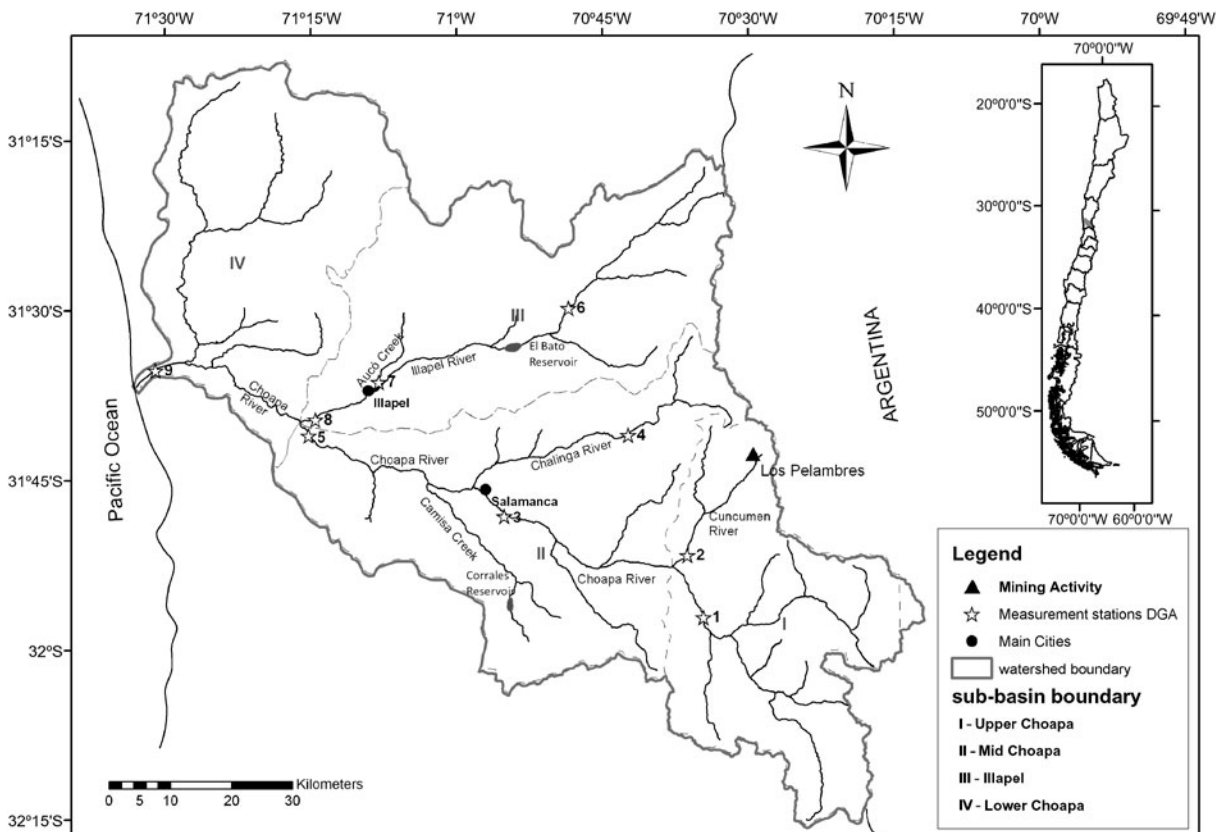
The approach followed by this study was oriented to obtain a general understanding of the natural and cultural factors responsible for the levels of pollutants, in particular those lithology- and mining-related, in the Choapa river basin. Thus, the major objectives are: (a) to assess ranges and average values of selected elements which are more affected by geological–mineralogical conditions as well as by current and past mining activities; (b) to evaluate possible relationships between the contents of these parameters and local hydrological conditions (precipitations, river discharges); and (c) to compare the obtained results with the neighboring Elqui river basin, which present similar geological and mining conditions.

## Materials and methods

### Study area

The Choapa river basin is located in the Coquimbo Region, North Central Chile, between 31°10' to 32°15' S and 70°16' to 71°33' W, covering an area of 7,630 km<sup>2</sup> from the Andes Cordillera to the Pacific Ocean (Fig. 1). Similar to other watersheds of the tectonic segment of the Transverse Valleys of North Central Chile (26°–33° S realm), it lacks a central N-S tectonic graben, which is present in most of the Chilean territory, north and south of this region (Oyarzún and Oyarzún 2010).

The Choapa river basin can be divided into four sub-basins: Upper Choapa river (1,560 km<sup>2</sup>), Middle Choapa river (2,247 km<sup>2</sup>), Illapel river (2,055 km<sup>2</sup>), and lower Choapa river (1,768 km<sup>2</sup>). The Choapa is the main river of the system, flowing from the Andean mountains to the Ocean



**Fig. 1** Choapa watershed with the different sub-basins, main rivers, tributaries and water reservoirs, cities, and DGA monitoring stations considered in this study (1 Choapa at Cuncumén, 2 Cuncumén before Choapa, 3 Choapa at Salamanca, 4 Chalinga at La Palmilla, 5 Choapa at Puente Negro, 6 Illapel at Las Burras, 7 Aucó before Illapel, 8 Illapel at El Peral, 9 Choapa at Huentelauquén)

in a SE to NW direction. The main tributaries, both in terms of drainage area and discharge (Cuncumén, Chalinga, and Illapel rivers), come from the NE. Most of them have their headwaters in the Andean range. Since this part of the Chilean territory is one of the narrowest of the country, rivers show steep gradients (ca. 2.5% in average) and turbulent flows. Also, some low-flow, non-permanent creeks, such as the Aucó and Camisas streams in the central part of the basin, are important to be considered, as explained below.

In the Choapa basin, precipitations concentrate from May to August. Average annual rainfall ranges from 200 to 450 mm (a “normal” year registers rainfall averages of ca. 240 mm in the watershed), being higher in the upper parts of the basin. Also, precipitation amounts increase two- or threefold on El Niño (ENSO) years, whereas the opposite situation occurs on La Niña dry years

(Dorsch et al. 2001; Favier et al. 2009). Normally, rivers attain their peak discharge on November to January, due to thawing processes of upper basin accumulated snow, ranging (for a 50% excess probability) from 1 to 20 m<sup>3</sup> s<sup>-1</sup> (DGA 2004).

Regarding geology, the watershed is mainly formed by Paleozoic granitoids and metamorphic rocks, and by mesozoic granitoids and volcano-sedimentary strata of calc-alkaline affinity, arranged in north–south belts which include marine sedimentary strata of Jurassic to Lower Cretacic age. The metallic ore deposits are distributed in association with these intrusive–extrusive belts, like the Illapel intrusive Super-unit, of Cretacic age (Rivano and Sepúlveda 1991). However, the principal metallic pulse at 10 Ma, responsible for the Los Pelambres porphyry, is Upper Miocene in age (Atkinson et al. 1996).

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Los Pelambres is a Cu (Mo) porphyric deposit, emplaced in a dioritic to granodioritic intrusive complex, crossed over by several small quartz-feldspatic porphyric bodies. The district is located in the headwaters of the Los Pelambres river, between 3,100 and 3,600 m altitude, 45 km NE from the town of Salamanca. Mined as an open pit, Los Pelambres is by far the largest mining operation of the Coquimbo Region, and therefore, of the Choapa Province (Fig. 2). Also, it is one of the most important at the national level, representing, in average for the 2000–2008 period, ca. 6% of the total Chilean Cu production and 25% of the Chilean Mo production (COCHILCO 2009). The deposit area has historically exhibited rather low pH's and significant levels of heavy metals on surface waters. Indeed, Los Pelambres is a Spanish name due to the fact that animals got their legs lacerated by surface water when pasturing in the area.

Also, small-scale mining activity in the basin is developed in the nearby of Illapel city, existing several mining operations for Cu and Au, most of them placed close to the Aucó creek. Due to this activity, many tailing and waste rocks deposits are scattered near Illapel, placed close to water courses of permanent and eventual flowing creeks.

Given all the mentioned factors, an active public concern about the effect of the mining activity on the water quality of the Choapa river exists. Also, the experience gathered at the hydrothermally altered El Indio mining area, some 250 km

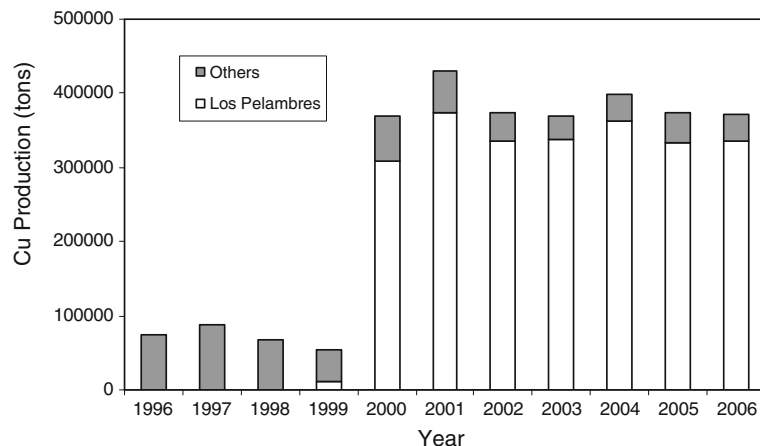
to the north, in the headwaters of the Elqui river basin, placed in the same and contemporary N-S metallogenic belt, is a reason to worry about. There, mining works enhanced the occurrence of natural processes resulting in extensive acid drainage generation, very low pHs, and high levels of As, Cu, and Fe on the waters of the Andean tributaries (Malo and Toro rivers), even after the mine closure (Guevara et al. 2006; Oyarzun et al. 2006; Galleguillos et al. 2008).

### Sampling and analysis

The information of surface water quality considered in this study corresponds to the 1980–2004 period and, given the objectives of this work, it focused on pH, electric conductivity (EC),  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , As, Cu, and Fe. It was provided by the Chilean Water Authority (Dirección General de Aguas, DGA), and came from nine monitoring stations placed throughout the basin (Fig. 1). Although records date back to 1980, there are some gaps in the historical data that differ on each station, and the sampling frequency varies between stations and years as well (e.g., there are years registering five samples whereas other years just have three or four samplings events).

The DGA sampling operation includes river discharge measurements. The procedure begins with the intake of unfiltered water samples in 0.5-L plastic bottles which are sent to the Environmental Laboratory of DGA at Santiago, where

**Fig. 2** Annual Cu production by Los Pelambres and other mining companies in the Coquimbo region (own elaboration from data of COCHILCO 2009)



they are preserved (refrigerated) until their analysis. Major anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ) are analyzed after filtering (0.45  $\mu\text{m}$ ). The same filtered solution is used for pH and EC determinations. For trace elements, the sample is acidified with 1 ml of concentrated  $\text{HNO}_3$  per 50 ml of sample and heated if turbidity is present. Filtering and analysis is done afterwards. Therefore, Fe, Cu, and As contents associated with suspended fine material could be incorporated into the analyzed solution.

The DGA Laboratory follows the analytical procedures described in Eaton et al. (1995). Quality control include internal checking (accuracy, precision), where every 3 months DGA receives and analyzes blind samples of known composition. Also, DGA is subjected to periodical audits by Chilean institutions like the INTEC-Chile (Corporación de Investigaciones Tecnológicas de Chile-CORFO) and CESMEC (Centro de Estudios, Medicion y Certificación de Calidad), and foreign institutions such as the Canadian GEMS (Global Environmental Monitoring System). Precision (expressed in terms of the standard deviation) for major elements is  $\pm 3\%$ , whereas that for trace elements is  $\pm 5\%$ . As, Cu, and Fe are analyzed by atomic absorption, with detection limits of 0.01, 0.01, and 0.03  $\text{mg l}^{-1}$ , respectively. Sulfate is analyzed by the turbidimetric method ( $\text{BaCl}_2$ ), with a detection limit of 2  $\text{mg l}^{-1}$ . Finally,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  are analyzed by titration and volumetric method respectively, with a detection limit of 1  $\text{mg l}^{-1}$  (F. Astudillo and F. Aguirre, DGA Laboratory, personal communication).

Chemical data was processed by univariate and bivariate statistical methods, and is presented in tables and graphical forms. As references for comparisons, both the Chilean standard for irrigation water, NCh 1333. Of78 (INN 1987) and the data obtained in previous studies in the Elqui watershed (Guevara et al. 2006; Galleguillos et al. 2008) were considered in the interpretation and discussion of results.

## Results and discussion

### General assessment

Table 1 shows the average values for the selected parameters in the different sub-basins and sampling stations for the period covered (1980–2004). When compared to the NCh 1333 (irrigation water quality standard), waters of the Choapa basin exhibit a rather good quality and the different parameters satisfy the thresholds defined by the regulation. The only exceptions are Cu and, in minor extent,  $\text{SO}_4^{2-}$  and EC values in the Cuncumén river, and EC and sulfate values in the Aucó creek. The results are presented in detail for each sub-basin and discussed in the following paragraphs.

### Upper Choapa sub-basin

The Cuncumén river receives water from the drainage area of the Los Pelambres district, a

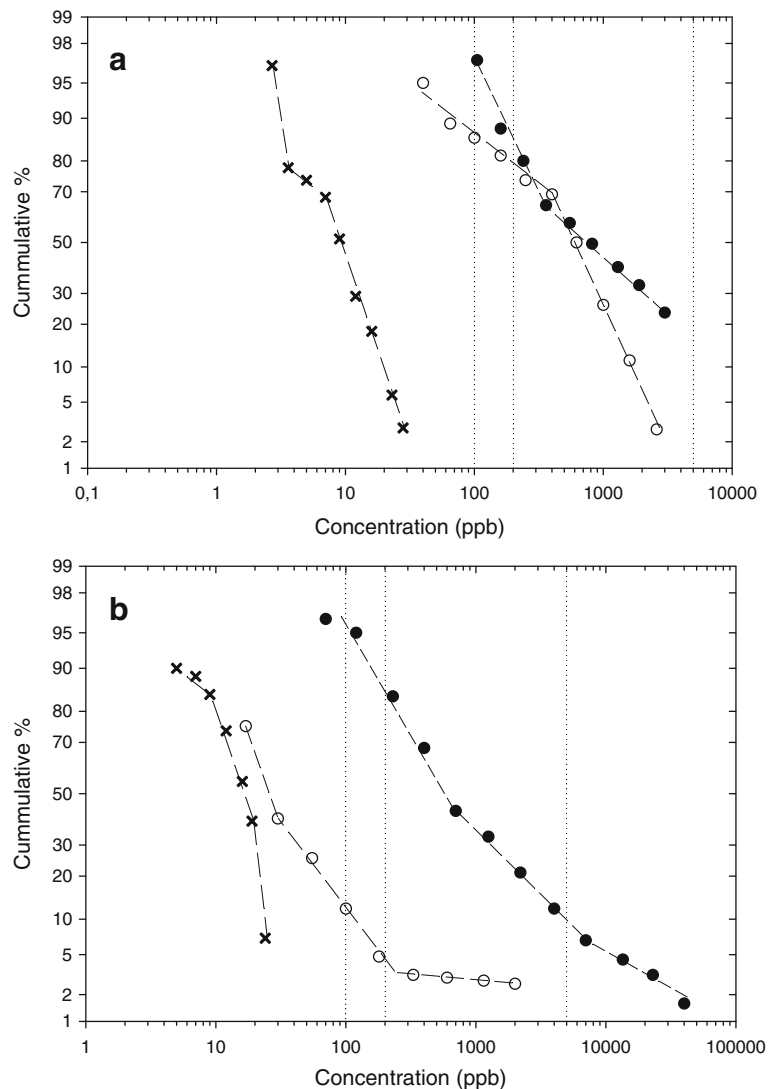
**Table 1** Average values for selected parameters (in  $\text{mg l}^{-1}$ ; EC in  $\mu\text{mhos cm}^{-1}$ ) during the period of study (n.a., not available)

Sub basin	River	pH	EC	$\text{HCO}_3^-$	$\text{Cl}^-$	$\text{SO}_4^{2-}$	As	Cu	Fe
Upper Choapa	Choapa at Cuncumén	7.7	240.1	69.8	8.6	44.9	0.013	0.072	1.571
	Cuncumén before Choapa river	7.6	475.2	61.5	21.8	165.6	0.008	0.474	0.881
Mid Choapa	Choapa at Salamanca	7.9	322.3	109.2	2.1	51.1	0.009	0.030	1.576
	Chalinga at La Palmilla	7.7	229.3	83.1	9.0	36.1	0.009	0.013	0.381
Illapel	Choapa at Puente Negro	8.1	397.5	145.4	17.0	54.7	0.005	0.028	0.853
	Illapel at Las Burras	7.5	150.6	56.6	4.7	18.6	0.003	0.014	0.439
	Aucó creek before Illapel river	7.7	1,073.0	178.5	25.4	377.8	0.004	0.04	0.756
	Illapel at El Peral	8.1	556.8	188.2	21.5	93.3	0.006	0.021	0.382
Lower Choapa	Choapa at Huentelauquén	8.3	419.1	146.6	20.8	62.6	0.004	0.013	1.217
NCh 1333		5.5–9.0	< 750	n.a.	< 200	< 250	< 0.1	< 0.2	< 5

fact which is clearly reflected in its high Cu content. When analyzed in a log-prob plot (Lepeltier 1969), it is observed that only 22% of the samples are under the NCh 1333 threshold (Fig. 3a). The distribution presents a negative break close to the 70% frequency percentage. The population presenting lower contents (between 0.04 and 0.4 mg l<sup>-1</sup>) includes a 32% of the samples analyzed. The second and principal population, assembling the 68% of the data, is over 0.4 mg l<sup>-1</sup> and clearly they are not in compliance with the NCh 1333. Arsenic exhibits a bi-modal distribution, including a middle segment representing low to moderate contents, originated in a mixture of

low and high As values. However, for this element, the high population does not exceed the limit established by the standard for irrigation water. The Cu and As diagrams exhibit an interesting parallelism as, in both cases, the upper population is defined by a break up close to the 70% percentage. This fact suggests that the higher Cu and As contents relate to a source in common, the porphyry copper mineralization affecting the upper course of the Cuncumén river, which receives surface and underground water from the Los Pelambres river. Finally, the Fe distribution presents a positive break close to 64% also suggesting the existence of two different populations.

**Fig. 3** Log-probabilistic diagram showing the distribution of As (*multiplication symbol*), Cu (*open circle*), and Fe (*close circle*). **a** Cuncumén river (1986–2004); **b** Choapa river at Cuncumén (1980–2004). Vertical lines represent the threshold value defined by the NCh 133 regulation for, from left to right, As, Cu, and Fe



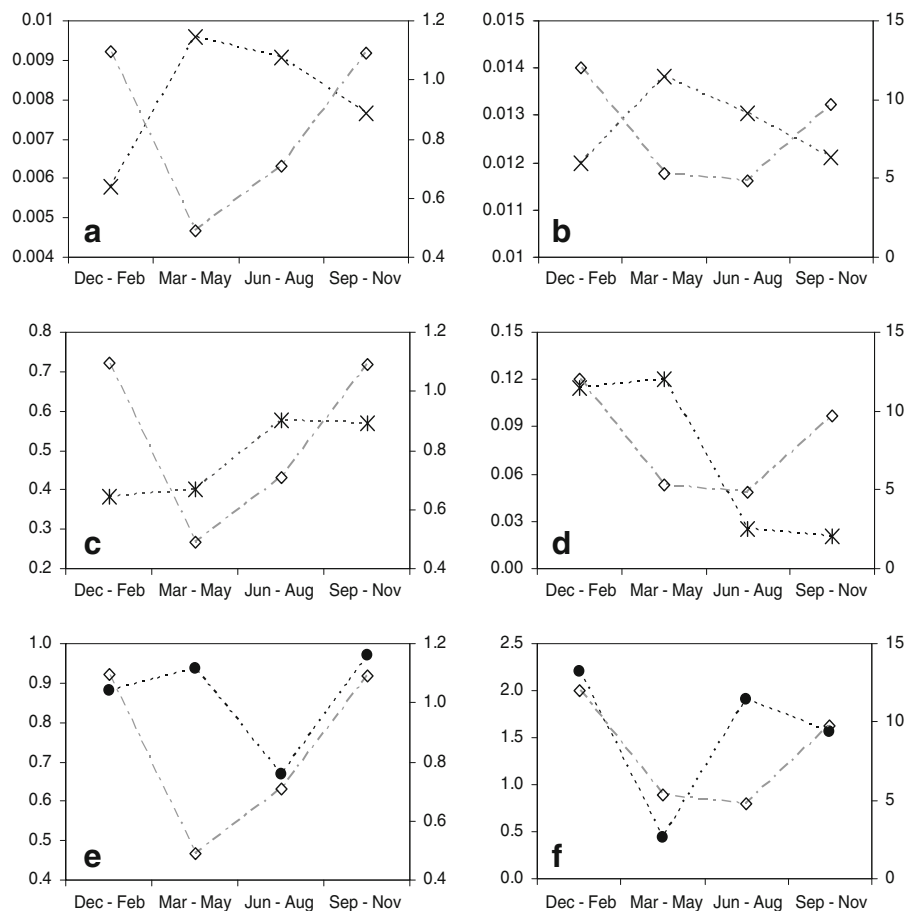


The local influence of the Los Pelambres district highlights when the Cu contents of the Cuncumén river water are compared with those of the Choapa river at its confluence point (Fig. 3b). While over a 70% of the historical data series of the Cuncumén river exceed the irrigation standard for copper, this situation occurs only for a 5% of the data at the Choapa river. Arsenic distribution exhibit two negative-sloped break points. The second segment includes most of the data (45%), with less dispersion than the other two segments. Finally for iron, unlike the situation described for the Cuncumén river, ca. only 10% of historical data exceed the NCh 1333 limit.

Considering the seasonal behavior of As, Cu, and Fe water contents data for the Choapa and Cuncumén rivers, different relationships emerge (Fig. 4). Thus, As concentrations present an in-

verse response to river flow, probably as a result of dilution after the increase in water flow due to snow melting in spring and summer. In exchange, Cu exhibits a more complex behavior, less dependent of the dilution effect, probably due to an increased contribution by fine suspended sediments. Indeed, sediment mass flux grows during high runoff period, the latter occurring due to spring–summer snow melting and occasional episodes of heavy rains in winter. In turn, Fe concentrations exhibit the largest increase in the snow-melting periods, between September and February, which could be due to the increase in turbulence resulting from the higher discharge, favoring the removal of Fe from the bottom sediments, transferring the metal to the water column. A similar situation for Cu and Fe was described by Guevara et al. (2006) for the neighboring Elqui river basin.

**Fig. 4** Tri-month averages As (*top panels, a and b*), Cu (*middle panels, c and d*), and Fe (*bottom panels, e and f*) concentrations for the Cuncumén river (*left panels, a, c, e*) and the Choapa river at Cuncumén (*right panels, b, d, f*). In the plots, the left Y-axis represent element (As, Cu, or Fe) concentration ( $\text{mg l}^{-1}$ ) and the right Y-axis the discharge (*open diamond*;  $\text{m}^3 \text{s}^{-1}$ )



Regarding sulfate, its historical average do not exceed the rather tolerant irrigation water standard ( $250 \text{ mg l}^{-1}$ ; Table 1). However, the standard was surpassed in a majority of the 2003 (50%) and 2004 (100%) samples of the Cuncumén river, probably due to the combined effect of a reduction in those year rainfall precipitations (and therefore in runoff) and an increase in the mining activity (Los Pelambres full production started in 2000). It is important to note that sulfate contents, as those of Cu, As, and Fe, are related to the presence of hydrothermal alterations, sulfide ore deposits and metallurgical activities. However, sulfate dispersion is less restricted by the solubility of its anionic form than As, and it is not affected by the hydrolytic constraints that strongly limit the concentration of Cu and Fe in neutral or basic water. Therefore, sulfate content is a better indicator of the influence of geology or mining activity on the chemical quality of surface or groundwater.

#### Middle Choapa basin

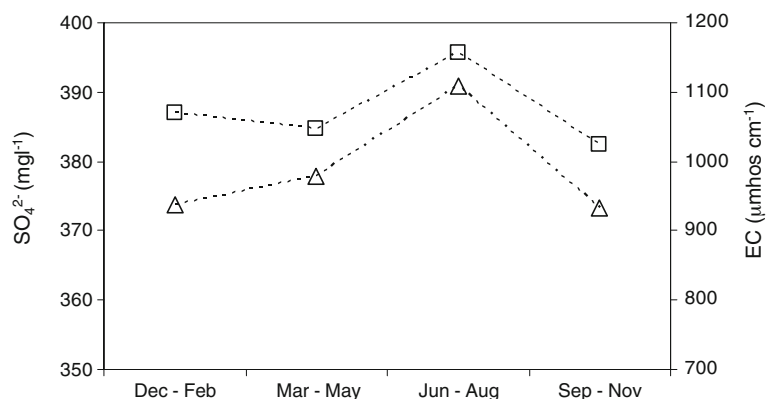
As shown in Table 1, the average values of the different parameters are adequate for the use of the river water for irrigation purposes in the middle part of the Choapa basin. In fact, more than 94% of the data fulfill the standard requirements for pH,  $\text{SO}_4^{2-}$ , CE,  $\text{Cl}^-$ , As, Cu, and Fe. This fact is a consequence of the resilience of the Choapa river to the pollution contributed by the Cuncumén river, for the average discharge of the former tends to be ca. tenfold higher than the

latter. Also, it illustrates the rather moderate extent of this contribution, despite the magnitude of the Los Pelambres deposit and the high tonnage of the mining operations carried out on the district. This important subject will be later examined in detail.

#### Illapel river sub-watershed

As previously mentioned, this sub-basin presents different water qualities depending on the presence of ore deposits, hydrothermal alteration zones, or mining operations on its drainage areas. Thus, for the Illapel river at Las Burras sampling station, the data indicates very good water quality. Fe content is the only parameter exceeding the standard, but only for a 1% of the historical data set. A different situation is registered for the Aucó creek, where average values of sulfate and EC, which present a good correlation, exceed the irrigation water standard (Fig. 5). The Aucó stream drainage zone is heavily mineralized and widespread Au and Cu small-scale mining has been carried out. Therefore, high sulfate contents are probably consequence of the oxidation of pyrite and Cu sulfides, either in situ or in the waste deposits left by the mining activities. In spite of its low discharge compared to that of the Illapel river (in the order of 1:10 to 1:100), the influence of the sulfate contribution of the Aucó creek is important, as detected downstream in the Illapel river, even at the El Peral monitoring station. Additional pollution sources are the several mining

**Fig. 5** Tri-month averages sulfate (*open triangle*) concentrations and electric conductivity (*open square*) levels at the Aucó creek





waste deposits close to the river and the town of Illapel. Sulfate contents attain peak values in this watershed during winter season (June–August), when most precipitations occur and contribute to dissolve  $\text{SO}_4^{2-}$  from oxidized waste piles.

Regarding As–Cu–Fe, the analysis of the historical data present a small percentage of Cu and Fe values exceeding the irrigation standard (Fig. 6). Moreover, As and Cu present similar distributions, which point to a common source. Indeed, this trait may be explained by the presence of sulfo-minerals such as enargite ( $\text{Cu}_3\text{AsS}_4$ ) in the local ore deposits.

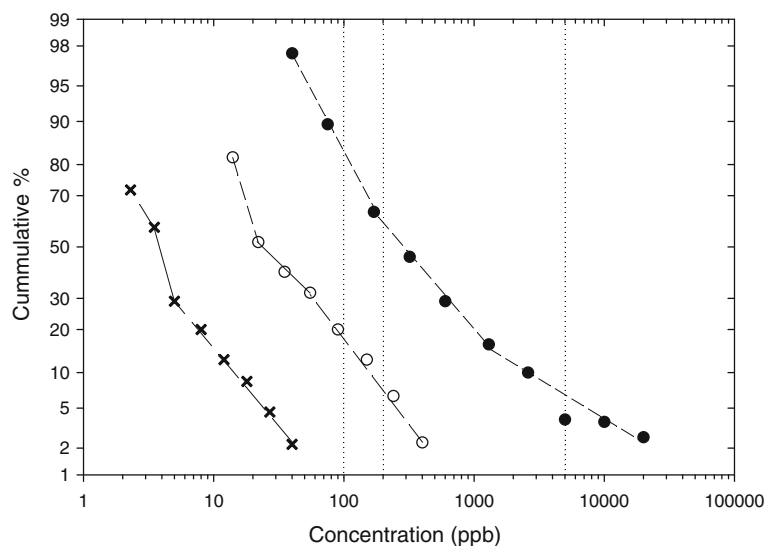
### Lower Choapa sub-basin

The historical data series for the Rio Choapa in Huentelauquén station exhibit water quality adequate for irrigation according to the NCh 1333 standard. More specifically, EC is related to the principal three anions,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ , which correlate negatively with runoff (Pearson coefficients of  $-0.65$ ,  $-0.62$ , and  $-0.78$ , respectively). In exchange, Cu, As, and Fe increase with higher runoff, a fact that suggests a possible influence of the fine sediments of the river bottom, which are removed and probably transfer its metallic content to the water column due to turbulent flow conditions.

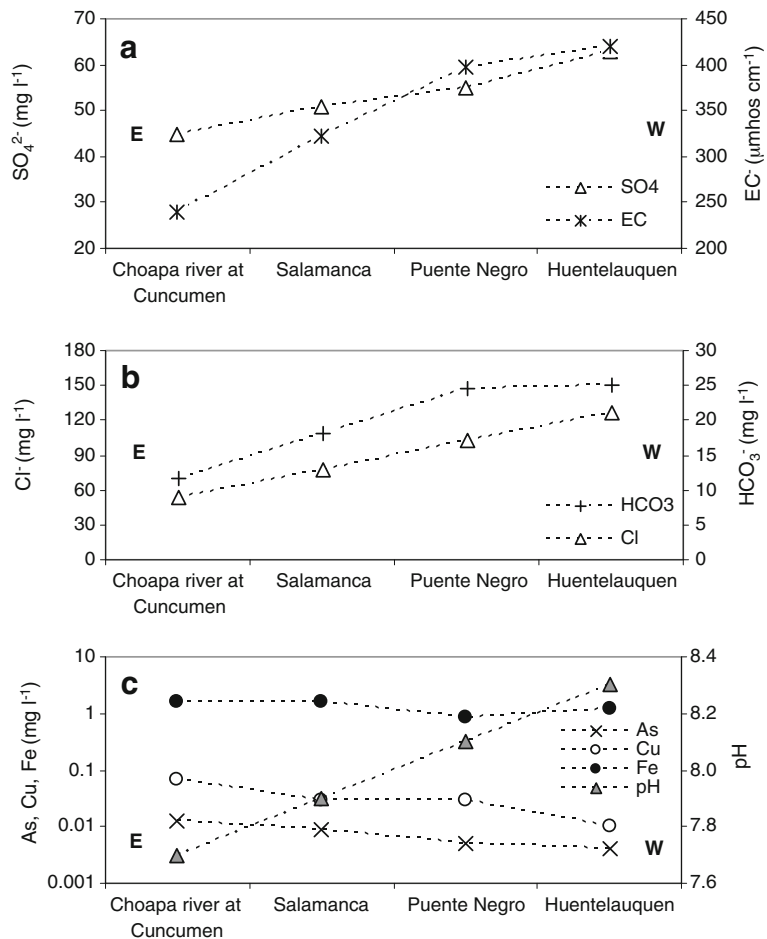
### Integrated assessment

Considering the whole Choapa basin, a number of interesting relationships appear. A first one is the downstream increase, from east to west, in sulfate content and EC (Fig. 7a). This increase, which is specially marked during the autumn and winter seasons, may be related to several factors, namely: (a) sulfate contamination due to natural inputs along the basin (hydrothermal alteration zones, sulfate sedimentary deposits); (b) sulfate pollution due to mining–metallurgical operations and wastes, or agricultural activities; and (c) sulfate concentration due to progressive water evaporation. The increase in sulfate content is accompanied by that of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  (Fig. 7b). In the case of  $\text{Cl}^-$ , the ocean is a well-known source, and the contribution of marine aerosols naturally increases with the proximity to the coast. Besides, it is likely that the presence of Neogene coastal marine sediments also contribute to higher saline contents (Rivano and Sepúlveda 1991). Both As and Cu contents (Fig. 7c) present an inverse behavior, decreasing westward. For Fe, a rather irregular behavior is observed. Average pH increase downstream in the basin, a fact that may be explained by the natural alkalinity of soils in arid basins. Water evaporation also contributes to this situation, as well as the presence of Neogene carbonate-rich sediments close to the

**Fig. 6** Log-probabilistic diagram showing the distribution of As (multiplication symbol), Cu (open circle), and Fe (close circle) for the Aucó creek (1984–2004). Vertical lines represent the threshold value defined by the NCh 133 regulation for, from left to right, As, Cu, and Fe



**Fig. 7** Downstream variation in sulfate and electric conductivity (**a**), bicarbonate and chloride (**b**), and As, Cu, Fe, and pH (**c**) at the Choapa basin (*E* east, *W* west)



coast (Dorsch et al. 2001). As already stated, the alkalinity of water favors the retention of heavy metals in the fine fraction of the rivers sediments (Brookins 1988; Oyarzun et al. 2007).

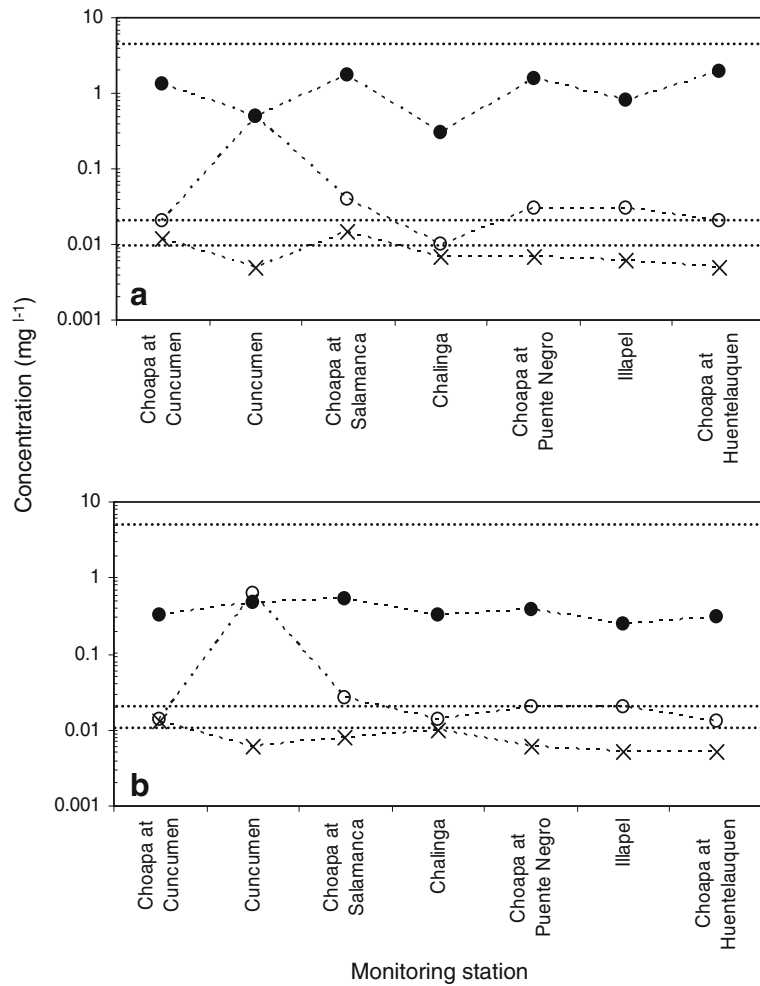
Regarding inter-annual variations and the effect of the water regime (e.g., “wet vs. dry” years) an in-depth analysis show some slight differences in As, Cu, and Fe contents, although they are not consistent throughout the watershed (Fig. 8). Basically, Fe shows the greater variation, decreasing some 54% in average in dry years compared with rainy years. In exchange, As and Cu increase about 10%, in average, in rainy years.

Finally, when comparing the situation of the Choapa basin with that of the Elqui river basin, some 180 km to the north, remarkable contrasts arise. Indeed, despite the similarities between the Elqui and Choapa basins in aspects such as geology, geomorphology, hydrology, the existence of

important mining districts in the basins headwaters (El Indio at Elqui, Los Pelambres at Choapa), and associated recent or current mining activities, there is an important and unexpected difference in terms of the metal content in surface waters, in particular in the Andean tributaries (Table 2).

El Indio Au–Cu–(Ag)–As district (29°46′ S, 69°59′ W; 3,500–4,000 masl), gathers a number of epithermal vein type deposits, being El Indio the major one, followed by Tambo and smaller deposits (Jannas et al. 1999). Their host rocks present different types of hydrothermal alteration, which is advanced argillic at Tambo, sericitic at El Indio, and propylitic at Rio del Medio. Besides, more than 30 hydrothermal alteration zones are displayed on the N–S belt that encloses the ore deposits, several of these zones of the advanced argillic type, with kaolinite, alunite, and silica jaspers. On the other hand, the Los Pelambres

**Fig. 8** Comparisons of As, Cu, and Fe in rainy (a average rainfall 492 mm year<sup>-1</sup>) and dry (b average rainfall of 95 mm year<sup>-1</sup>) years throughout the watershed. Horizontal dotted lines represent, from bottom to top, NCh 1333 limits for As, Cu, and Fe



porphyry deposit (31°43' S, 70°29' W; 3,500 masl) is hosted by a quartz diorite belonging to the Infiernillo Miocene unit, the same unit responsible for the El Indio district (Atkinson et al. 1996). The partly popyric quartz diorite is em-

placed in the Cretaceous Los Pelambres volcanic-sedimentary formations (Rivano and Sepúlveda 1991). Los Pelambres has a central potassic alteration core, surrounded by quartz-sericitic alteration of the intrusive rocks and a large propylitic

**Table 2** Comparison of chemical parameters (mg l<sup>-1</sup>, electric conductivity in  $\mu\text{mhos cm}^{-1}$ ) in the rivers of the Elqui and Choapa basins under the influence of the El Indio (Toro, Turbio, Elqui) and Los Pelambres

River	Parameter					
	pH	EC	SO <sub>4</sub> <sup>2-</sup>	Cu	Fe	As
Toro River [1]	5.1	1,756	843	5.60	22.0	0.83
Turbio River [1]	7.5	673	198	1.05	5.4	0.15
Elqui River [1]	7.8	737	152	0.47	3.4	0.04
Cuncumén River [2]	7.6	475	166	0.47	0.9	0.008
Choapa River [2]	7.9	300	47	0.05	1.4	0.06
World average [3, 4]	n.a.	n.a.	11.2	0.007	0.05	0.0006

(Cuncumén, Choapa), respectively (References: [1] Oyarzun et al. (2006); [2] this study; [3] Allegre and Michard (1973); and [4] Levinson (1974); n.a., not available)

zone developed in mafic andesites. Whereas Los Pelambres before mining ore reserves were around 3,000 Mt, about 20 to 30 times bigger than those of El Indio district, the latter has been responsible for a major case of Cu and As pollution in the Elqui river (Oyarzun et al. 2006; Galleguillos et al. 2008), which greatly surpass the effect of Los Pelambres on the Choapa basin. Relatively low to moderate Cu contents of the Choapa river water could be explained by its neutral to basic pH conditions, responsible for metal transference from water to fine-grained sediments, due to  $\text{Cu}^{2+}$  hydrolysis. However, when compared to the metal contents of the Elqui river sediments, those of the Choapa river are also moderate (for Cu, about 20% of the Elqui river sediments contents, Table 3).

This apparent paradox could not be explained solely in ore mineralogy terms, as both districts contain pyrite, a major ARD agent; besides, they also share geological, hydrological, and climate conditions. However, the fact that El Indio is located in a belt presenting widespread advanced argillic alteration, in contrast to the moderate hydrothermal alteration affecting the mafic host rocks of the Los Pelambres district, delivers an important clue. Indeed, mafic rocks, containing minerals like pyroxene and Ca-plagioclase, react with ARD, and therefore perform as buffers (Oyarzun et al. 2007; Oyarzún et al. 2009). However, this buffer property is destroyed by advanced hydrothermal alteration, as occurs in the El Indio district. This principle has been recently illustrated by the case of the development of an alkaline-rich lake in pyrite-rich rocks, but affected by Na metasomatism, in the Mother Lode Gold District in California (Savage et al. 2009), and by the fact that the higher rate of ARD generation in the Butte-Montana District is related to the zone

of advanced argillic alteration (Gammons et al. 2009).

Finally, fracturing is rather moderate at Los Pelambres when compared to the situation of El Indio, a fact that helps to prevent acid rock drainage dispersion and widespread distribution.

## Conclusion

In general, surface waters exhibit a rather good quality in the Choapa river basin although high Cu levels are found in the upper parts of the watershed, near the Los Pelambres deposit, and in the Aucó stream (in addition to high sulfate content for the latter). Besides mining activity, natural conditions are also important factors determining the composition of waters. Despite the importance of the Los Pelambres deposit and related mining activity, there is not a major case of Cu and As pollution in the Choapa basin, unlike the situation described for the neighboring Elqui watershed.

Acid drainage generation is a key factor in assessing the environmental impact of mining projects, as well as in the estimation of future cost and effectiveness of closure plans of current and new mining operations. If the buffering properties of mafic igneous rocks affected by propylitic alteration (which are widespread in the Chilean and Andean geology) is neglected, acid drainage assessment risks may be overestimated, and therefore the costs and focus of its control. On the contrary, highly fractured rocks affected by advanced argillic alteration could implicate a major and permanent problem in terms of acid drainage, especially when located at the headwaters of river basins. The cases presented and analyzed in this

**Table 3** Cu, Zn, and As contents ( $\text{g t}^{-1}$ ) of the Choapa and Elqui river sediments (downstream from the Los Pelambres and El Indio source, respectively) (n, number of

sampling stations; References: [1] Oyarzun et al. (2007); [2] Oyarzún et al. (2003), average for four seasonal sampling)

	Cuncumén-Choapa rivers [1]				Toro-Turbio-Elqui rivers[2]			
	Range	Average	Median	n	Range	Average	Median	n
Cu	573–46	197	116	9	1,956–350	1,077	1,060	10
Zn	148–62	124	132	9	610–105	326	322	10
As	22–9	15	15	9	209–26	106	100	10

paper illustrate how this simple principle may be used (a) to discriminate different risks condition within a district, and (b) to compare risks between two districts located at similar geological and geographical contexts, but displaying opposite fracturing and hydrothermal alteration conditions. The fact that a pyrite-rich extremely large porphyry copper deposit like Los Pelambres had produced a rather moderate Cu pollution of its drainage basin, stresses the importance of the factors discussed in this work.

Finally, from the results in this study (as well as those of previous researches), it is important to state that the ARD generation potential of the Au–Ag Pascua-Lama epithermal district in the headwaters of the Huasco basin (29° S, 70° W, ca. 4,000 masl). This deposit, which is starting to be mined, should be monitored carefully, given the similarities in terms of the context, hydrothermal alteration and mineralogy between Pascua Lama and El Indio districts.

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