

The As-contaminated Elqui river basin: a long lasting perspective (1975–1995) covering the initiation and development of Au–Cu–As mining in the high Andes of northern Chile

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Received: 28 October 2005 / Accepted: 22 February 2006
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Abstract The Elqui watershed (northern Chile) constitutes a highly contaminated river system, with arsenic exceeding by up to three orders of magnitude the average for river waters. There are three main reasons that explain this contamination: (1) the

regional geology and hydrothermal (mineralizing) processes that developed in this realm during Miocene time; (2) the later unroofing–erosion–oxidation–leaching of As–Cu rich sulfide ores, a process that have been taking place for at least 10,000 years; and last but not least (3) mining activities at the high-altitude (>4000 m above sea level) Au–Cu–As El Indio mine, from the late 1970s onwards. The El Indio mineral deposit hosted large veins of massive sulfides, including the important presence of enargite (Cu_3AsS_4). The continuous natural erosion of these veins and their host rocks (also rich in As and Cu) during Holocene time, led to important and widespread metal dispersion along the river system. During the studied pre mining period (1975–1977), the high altitude river Toro waters already showed very large As concentrations ($0.36\text{--}0.52\text{ mg l}^{-1}$). The initiation of full scale mining at El Indio (1980 onwards) led to an increase of these values, reaching a concentration of 1.51 mg l^{-1} As in 1995. During the same year other rivers of the watershed reached peak As concentrations of 0.33 (Turbio) and 0.11 mg l^{-1} (Elqui). These figures largely exceed the USEPA regulations for drinking water (0.01 mg l^{-1} As), and about 10% of the total As data from the river Elqui (and 70% from the river Turbio) are above the maximum level allowed by the Chilean law for irrigation water (0.1 mg l^{-1} As).

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Keywords Arsenic · Contamination · Waters · Mining · Elqui watershed · Chile

Introduction

The Elqui watershed covers an area of about 9800 km², and its main river (the Elqui) constitutes one of the few water resources of this hilly, semi-arid region of Chile (Fig. 1). Most of the water is used for irrigation purposes, although an important part is also used to satisfy the urban needs of a population of 364,694 inhabitants (2002 census) (Comisión Nacional del Medio Ambiente, 2005), that live in the towns of La Serena and Coquimbo (Fig. 1). The region is characterized by a mountainous landscape and a semi-arid climate, with highly variable precipitations (Fig. 2a). Except for a discontinuous coastal narrow belt, the region is dominated by E–W oriented valleys, with rivers that flow from the Andean mountains to the coast. The main valleys, such as the Elqui, are flanked by mountain belts of about 50 km wide and altitudes of 600–1000 m above sea level. However, these are to be regarded as the ‘low-lands’, because the Andes, in a easternmost position, reach altitudes above 5000 m (Fig. 1). It is precisely within this high-altitude domain where the potential sources for arsenic contamination are located. Among these the

most important are the El Indio As-rich gold deposits and associated hydrothermal alteration zones (Fig. 1). Some of the mining works at El Indio reach 4400 m above sea level, and are only 125 km away from the coast, which creates a strong gradient of altitude. The El Indio mine is cross-cut by the river Malo (malo=bad) which is one of the easternmost tributaries of the Elqui watershed. The Malo is part of a high-altitude fluvial system (HAFS) of tributary rivers, comprising among others the Toro river, which together with the river La Laguna converge into the Turbio (Fig. 1), which is one of the main tributaries of the main river Elqui. River flows are in the order of: 0.55–1.1 m³ s⁻¹ (Toro), 0.7–4.5 m³ s⁻¹ (La Laguna), 5–12 m³ s⁻¹ (Turbio), and 8–25 m³ s⁻¹ (Elqui at Algarrobal), although these figures strongly increase during stormy episodes (flash floods). For example, the river Elqui can reach flows up to the order of 400 m³ s⁻¹. These are very shallow rivers, never exceeding 2 m of depth.

The HAFS is particularly relevant to the environmental setting of the Elqui watershed, because these rivers cross-cut a hydrothermal alteration belt and epithermal ore deposits/prospects. In other

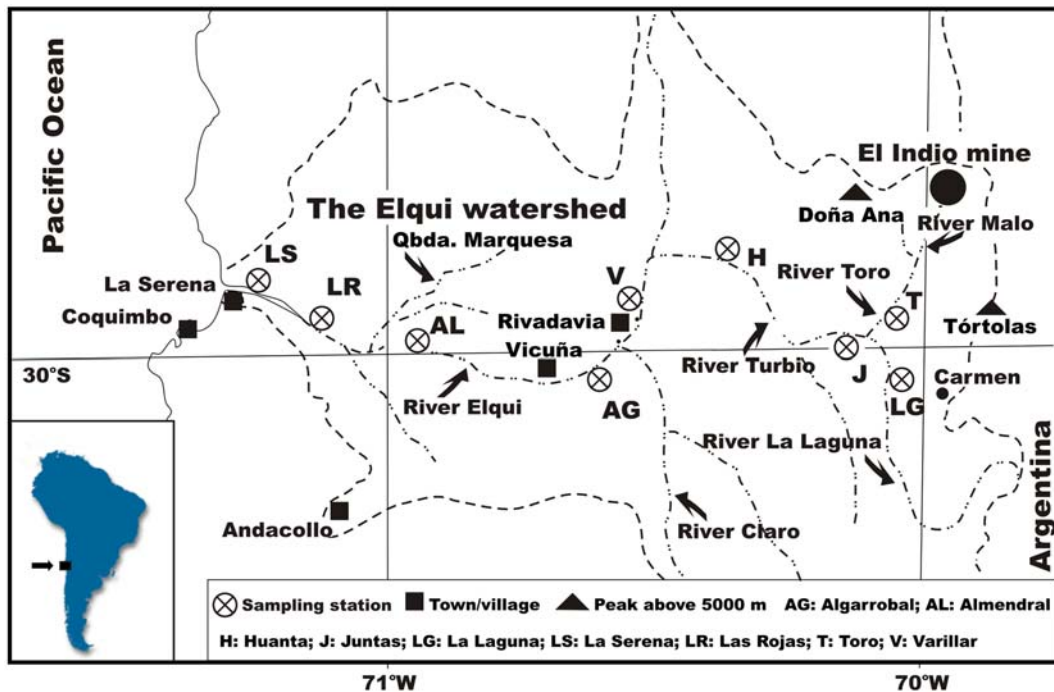


Fig. 1 The Elqui watershed, showing location of sampling stations. See inset for location of the studied area

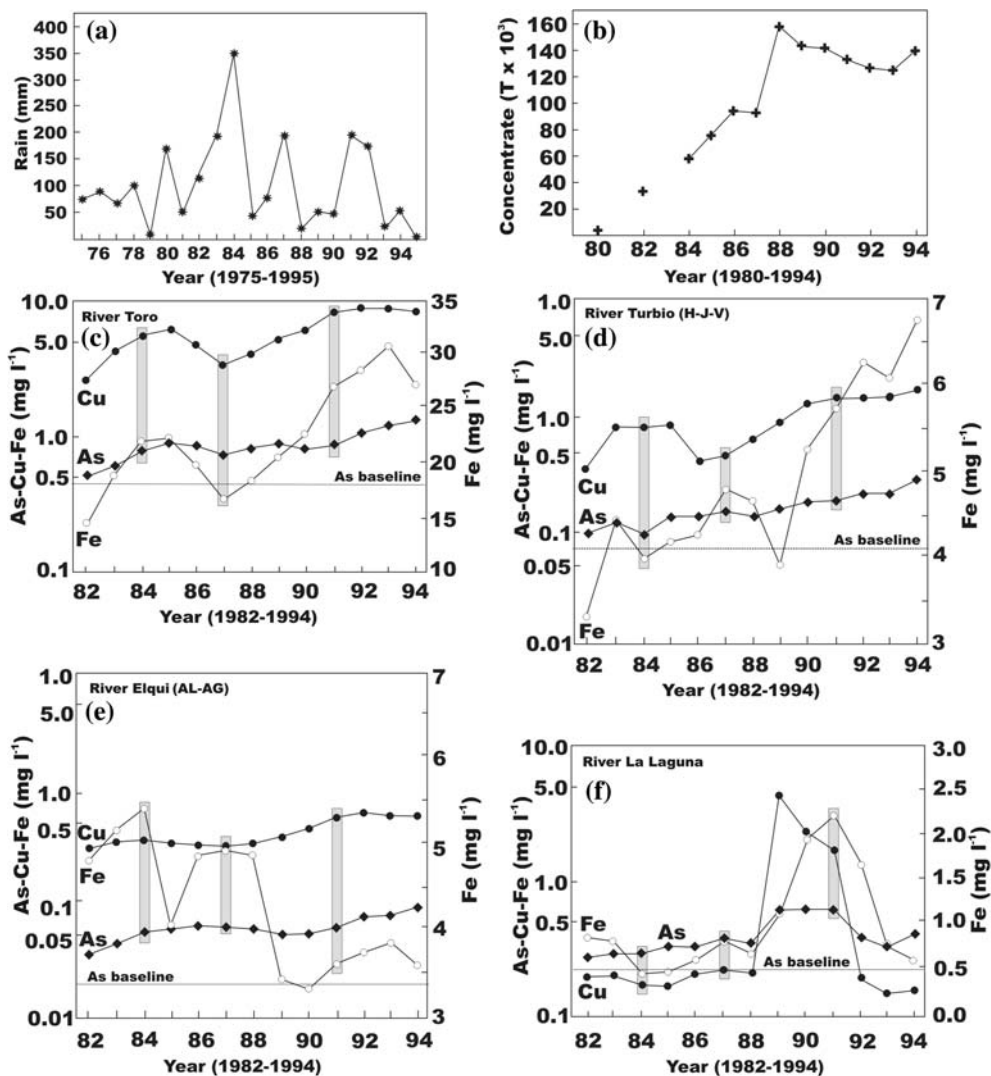


Fig. 2 (a) Precipitations during the period 1975–1995 (recorded in Rivadavia, see Fig. 1 for location). (b) Production of Au–Ag–Cu–As concentrate at El Indio. (c–f) As–Cu–Fe concentration (rolling means) in the waters of the rivers Toro,

Turbio, Elqui, and La Laguna, for the period 1982–1994. The As baseline corresponds to the mean value for the period 1975–1977. The shaded vertical bars correspond to rainy years (see also a)

words, the HAFS drains a source area anomalously rich in arsenic and copper (Oyarzun, Lillo, Higuera, Oyarzún, & Maturana, 2004). Different from other, pristine Chilean Andean rivers, the Elqui has severe environmental problems regarding heavy metals and As contents in both stream sediments (Oyarzun et al., 2004; Oyarzún, Maturana, Paulo, & Pasieczna, 2003) and waters (Dittmar, 2004; Guevara, 2003). We present the results of 20 years (1975–1995) of water quality monitoring of the Elqui river system, which provides a basis for the evaluation of

the potential environmental problems derived from the mining industry. The time series starts in 1975, before the initiation of the mining works at El Indio, and ends up in 1995, i.e., the time span covered by the data files recently disclosed by the Chilean Water Authority (CWA; Dirección General de Aguas de Chile). Taken into account the geology of this realm, the mineralogy of the El Indio ore deposits, and the metallurgical processes devised to obtain gold, silver, copper, and arsenic trioxide, we concentrated our efforts on three key elements: As,

Cu, and Fe. Other relevant parameters considered in this study are the sulfate content and pH. The results of this work follow.

Geology, mineral deposits, and mining activities

The geology of the Elqui watershed includes a variety of rock units ranging in age from Paleozoic to Quaternary. At a more local scale, the high-altitude domain of the region comprises a series of volcanic sequences of Cenozoic age, among which two are particularly relevant from the metallogenic point of view (Maksaev, Moscoso, Mpodozis, & Nasi, 1984): the Doña Ana Formation (Upper Oligocene-Lower Miocene), with rhyolites, rhyolitic tuffs, andesites and basaltic andesites, and the so-called Infiernillo Unit (Lower Miocene). More than thirty large hydrothermal alteration zones, including that of El Indio can be defined within a N–S belt of $\sim 200 \times 20$ km. Many of these zones comprise advanced argillic alteration mineral assemblages, with kaolinite, alunite, and silica jaspers. Another relevant feature in the study zone is a sequence of Early Holocene lacustrine sediments (9640 ± 40 years BP, AMS radiocarbon date), which occur as perched outcrops in the mountain slopes flanking the river Turbio for about 3 km. This +10 m thick sequence, with very high As contents of up to 2344 mg kg^{-1} , comprises alternating light colored clay–gypsum beds and dark carbon- and gypsum-rich horizons (Oyarzun et al., 2004).

Most relevant to this work is the short, however crucial history of gold mining in the HAFS. The El Indio deposit has a mining history (Lagos & Velasco, 1998) that initiates during the 1960s, however, the early mining works were of small-scale and no important activities took place until 1975 when the St. Joe Gold Corporation acquired the rights to the deposits. The deposit changed hands several times during the 1980s being first acquired by the Fluor Company (1981), then by the Alan Bond Group (1987), and finally by the Lac Minerals Ltd (now Barrick Gold Corporation). Data from Lago and Velasco (1998) for the El Indio mine (now closing) indicate that the extracted dry ore was sent to a plant with a capacity of 2600 td^{-1} (1988). The mineral underwent cyanidation and flotation. The copper concentrate contained 20% Cu, 50 gt^{-1} Au, 300 gt^{-1} Ag, and 8% As. The concentrate was later treated in a

roaster furnace to remove the arsenic. The gas generated was mixed with air to allow oxidation of As and S. The gas eventually passed through an electrostatic precipitator and it was mixed with cool air, which led to precipitation of arsenic trioxide (As_2O_3). The tailings of this first stage were then prepared for cyanidation to recover gold and silver.

Data acquisition and methods

We obtained the data for the different rivers of the Elqui system from the Chilean Water Authority (CWA; Dirección General de Aguas de Chile) (Guevara, 2003). The CWA has several monitoring stations (Fig. 1), and samples are usually taken on a monthly basis (pH, As, Cu, and Fe) or every 3 months (sulfate). That generated a large number of data comprising the periods 1975–1978 and 1981–1995 (Tables 1 and 2). The CWA follows the analytical procedures described in the work “Standard Methods for the Examination of Water and Wastewater” (Eaton, Clesceri, & Greenberg, 1995). The CWA procedures for water sampling include the following: the samples are filtered to $0.45 \mu\text{m}$ (laboratory-grade filters), and kept in plastic bottles of 0.5 l, which are refrigerated and sent to the central laboratories of the CWA (Santiago de Chile). Quality control include the following procedures. Internal checking (accuracy of results): every three months the CWA receives and analyzes blind samples of known composition to check procedures; external checking: the CWA is subjected to periodical checking (audits) by Chilean institutions such as the INTEC and CESMA, and foreign institutions such as the Canadian GEMS. Precision (expressed in terms of the standard deviation) for major cations and anions is $\leq 3\%$, whereas that for trace elements is $\leq 5\%$. As, Cu, and Fe are analyzed by atomic absorption, with detection limits of 0.01, 0.01, and 0.02 mg l^{-1} respectively. Sulfate is analyzed by the turbidimetric method (BaCl_2), with a detection limit of 0.001 mg l^{-1} . The field procedures for pH determinations are the following: water is collected from the river, filtered, and put into a clean plastic bottle, the portable instrument is rinsed before the analyses with deionized water, and the meter systematically recalibrated using appropriate solution standards.

Table 1 Number of samples, range and mean values for As, Cu, Fe, SO₄²⁻, and pH in the different rivers and sampling stations (see also Fig. 1) for the periods 1975–1995

River	La Laguna						Turbio								
	Toro (T)			La Laguna (LG)			Juntas (J)			Huanta (H)			Varillar (V)		
	n	Range	Mean	n	Range	Mean	n	Range	Mean	n	Range	Mean	n	Range	Mean
As	188	0.06–3.95	0.83	185	<0.005–0.90	0.04	153	0.01–1.26	0.21	109	<0.005–0.68	0.17	173	0.01–0.48	0.12
Cu	177	0.01–28.40	5.62	106	<0.01–5.88	0.08	134	0.02–7.36	1.43	109	0.02–6.26	1.00	166	0.02–3.92	0.71
Fe	173	0.20–87.80	21.89	169	<0.01–28.77	1.03	136	1.14–30.43	6.08	110	0.05–50.50	5.67	168	0.04–56.10	4.59
SO ₄ ²⁻	85	307.0–1161.0	843.34	81	43.2–192.0	96.00	76	97.5–486.5	235.01	34	74.0–557.0	205.88	69	62.40–284.30	164.89
pH	208	3.91–7.60	5.11	209	4.45–8.67	7.62	177	6.15–8.66	7.24	111	6.60–8.20	7.51	190	6.40–8.25	7.69
River	Elqui			Almendral (AL)			Las Rojas (LR)			La Serena (LS)					
Station	Algarrobal (AG)			Almendral (AL)			Las Rojas (LR)			La Serena (LS)					
As	73	0.01–0.30	0.07	157	<0.005–0.27	0.04	24	<0.005–0.08	0.03	48	<0.005–0.31	0.03			
Cu	67	0.01–1.45	0.41	149	0.01–1.00	0.22	25	0.01–0.54	0.15	46	<0.01–33.50	0.86			
Fe	67	0.13–27.50	3.0	151	0.06–68.50	2.70	24	0.10–4.30	0.87	51	0.06–156.00	4.43			
SO ₄ ²⁻	76	13.4–169.5	117.4	72	55.2–178.2	130.10	21	111.9–182.5	150.59	53	74.0–382.0	210.01			
pH	113	6.70–9.34	7.68	193	6.85–9.26	7.79	26	6.60–8.32	7.70	72	6.35–8.32	7.78			

Data for As, Cu, Fe, SO₄²⁻ in mg l⁻¹; n: number of data. For comparison: mean concentrations of As, Cu, and Fe from the river Turbio (at Juntas) in 2002 are the following: (1) As: 0.16 mg l⁻¹; (2) Cu: 3.72 mg l⁻¹; and (3) Fe: 7.79 mg l⁻¹ (Galleguillos, 2004)

Results and discussion

As, Cu, Fe, SO₄²⁻ in the river waters

The rivers Toro, Turbio, and Elqui (see sampling stations in Fig. 1) present a clear enrichment in As, either if we compare them to the world average for river waters (Gaillardet, Viers, & Dupré, 2004) or to the 1975–1977 local baseline concentration, and the same applies to Cu and Fe (Fig. 2c–e) (Tables 1–3). We observe a remarkable metal increase in the waters starting in the early 1980s, which coincides with the initiation of full-scale mining and metallurgical operations at El Indio (Fig. 2b). On the other hand, As, Cu, and Fe increase their concentration upstream, with the river Toro having the highest metal contents, a trend also observed by Dittmar (2004) for the period December 1992–October 1993. Given that the Turbio and Elqui rivers receive waters from other tributaries (Fig. 1), and therefore the metal concentration undergoes dilution, the Toro gives us the best picture in terms of the contamination derived from the mining operations. If we compare the figures of concentrate production and metal contents for the time span 1980–1985, a remarkable ascending trend can be observed for As, Cu, and Fe (Fig. 2c). This ascent is followed by a decrease in 1986, which matches a lowering in concentrate production. From there onwards production and metal contents follow different patterns. Peak production of concentrates was reached in 1988, however, despite the subsequent declining trend, the metal contents continued to increase in the waters, not only in the Toro, but also in the Turbio and the Elqui rivers. Although concentrate production (Figure 2b) gives us a proxy for contamination, there are other factors that also contribute to the disruption of the normal geochemical behavior of this realm. A first insight into this matter is provided by the river La Laguna (Fig. 1), which displays a remarkable increase in As, Cu, and Fe in the year 1989 (Fig. 2f). We investigated this matter and the most likely possibility for this anomaly was mining activity in this area. The initiation of the highly successful and profitable mining operation at El Indio brought a renewed interest in the area, thus in 1988 exploration/mining works were initiated at Carmen (Fig. 1), however, early contaminant restrictions imposed by ENAMI (a Chilean state owned mining company that explores, gives technical help to small companies, buy raw

Table 2 Mean annual concentrations (1975–1977, 1981–1995) and rolling means (1982–1994) for As, Cu, and Fe in the rivers Toro, Turbio, and Elqui

Year	1975	1976	1977	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995
<i>River Toro</i>																		
Mean concentration (mg l ⁻¹)																		
As	0.42	0.52	0.36	0.55	0.51	0.54	0.80	1.02	0.79	0.76	0.66	0.89	1.02	0.55	0.97	1.52	0.94	1.51
Cu	1.82	1.37	1.48	2.42	3.24	1.77	8.00	7.37	3.18	3.04	3.66	5.15	6.62	5.84	11.35	8.66	6.21	9.65
Fe	21.20	14.30	11.84	10.89	17.70	14.75	24.30	25.94	16.55	17.71	16.03	21.47	23.85	21.77	35.00	28.22	28.91	24.44
Rolling means (mg l ⁻¹)																		
As					0.54	0.62	0.78	0.87	0.86	0.74	0.77	0.85	0.82	0.85	1.01	1.14	1.33	
Cu					2.48	4.34	5.72	6.18	4.53	3.29	3.95	5.14	5.87	7.94	8.62	8.74	8.17	
Fe					14.45	18.92	21.66	22.26	20.06	16.76	18.40	20.45	22.36	26.87	28.33	30.71	27.19	
<i>River Turbio</i>																		
Mean concentration (mg l ⁻¹)																		
As	0.05	0.09	0.07	0.08	0.13	0.09	0.12	0.07	0.20	0.12	0.12	0.15	0.17	0.20	0.16	0.23	0.22	0.33
Cu	0.02	0.35	0.39	0.30	0.50	0.30	1.82	0.41	0.37	0.48	0.48	0.91	1.16	1.63	1.23	1.14	1.62	2.00
Fe	2.62	6.88	3.23	2.90	3.55	3.61	6.21	2.18	4.23	6.42	3.82	3.82	4.01	8.01	5.18	5.55	7.48	7.10
Rolling means (mg l ⁻¹)																		
As					0.10	0.11	0.09	0.13	0.13	0.15	0.13	0.15	0.17	0.18	0.20	0.20	0.26	
Cu					0.34	0.87	0.84	0.86	0.42	0.44	0.62	0.85	1.23	1.34	1.33	1.33	1.40	
Fe					3.35	4.46	4.00	4.21	4.28	4.82	4.69	3.88	5.28	5.74	6.25	6.07	6.75	
<i>River Elqui (AG-AL)</i>																		
Mean concentration (mg l ⁻¹)																		
As	0.01	0.03	0.02	0.02	0.03	0.05	0.05	0.06	0.06	0.06	0.06	0.05	0.04	0.05	0.07	0.08	0.06	0.11
Cu	0.02	0.15	0.17	0.11	0.22	0.26	0.32	0.26	0.17	0.22	0.20	0.31	0.31	0.41	0.56	0.51	0.31	0.57
Fe	1.10	2.15	1.60	1.64	0.74	9.14	4.91	2.12	1.88	8.13	2.99	1.33	1.18	2.23	2.97	1.86	2.88	2.54
Rolling means (mg l ⁻¹)																		
As					0.03	0.04	0.05	0.06	0.06	0.06	0.06	0.05	0.05	0.06	0.07	0.07	0.09	
Cu					0.20	0.27	0.28	0.25	0.22	0.20	0.24	0.27	0.34	0.43	0.49	0.46	0.46	
Fe					3.84	4.93	5.40	2.97	4.05	4.33	4.15	1.83	1.58	2.13	2.35	2.57	2.42	

All data in mg l⁻¹. AG: Algarrobal, AL: Almendral. The means are adjusted to two decimals (e.g., 3.8386 → 3.84)

minerals and concentrates, and refines copper), made this operation unfeasible, which explains the sudden drop in metal contents by the year 1992 in the river la Laguna (Fig. 2f). To understand why exploration works can lead to strong contamination in this region of Chile we have to explain the techniques that are the common practice in this realm. A typical operation would include intensive use of large bulldozers, that cut the loose regolith that cover the slope of the mountains (Fig. 3). This serves for two purposes: road building and geochemical sampling, the latter being a highly successful exploration tool in this realm. Given that the physiographic setting includes steep, typical Andean valleys, most if not all the material removed by the bulldozer goes directly to the bottom of the valley, thus contaminating the river (Fig. 3). Thus, taking into account that the area underwent continuous exploration (and mining development) during the 1980s, we may assume that at least part of metal content in the rivers was derived from this activity.

The pH values and SO₄²⁻ contents display a more complex and intriguing pattern (Fig. 4a, b). For example, given the proximity to the El Indio mine, one would expect a lowering of pH after large-scale production began, however, the Toro pH shows a tendency towards higher values from 1981 to 1995 (Fig. 4a), which may be related to the industrial introduction of flotation and cyanidation, processes that operate under alkaline conditions. Besides, part of the high SO₄²⁻ concentrations can be explained in terms of the dissolution of sulfate solid phases (e.g., gypsum), typical of the arid to semi arid environment of northern Chile (e.g., Oyarzun et al., 2004; Romero et al., 2003). On the other hand, the pH in the Turbio and Elqui rivers shows an erratic behavior, with first, a tendency towards lower values (1981–1984), and then an increase followed by a decrease in 1988. Given that the La Laguna river is a tributary of the Turbio, the initiation of mining works and exploration at Carmen in 1988 (Fig. 1) could explain the latter. In any case,

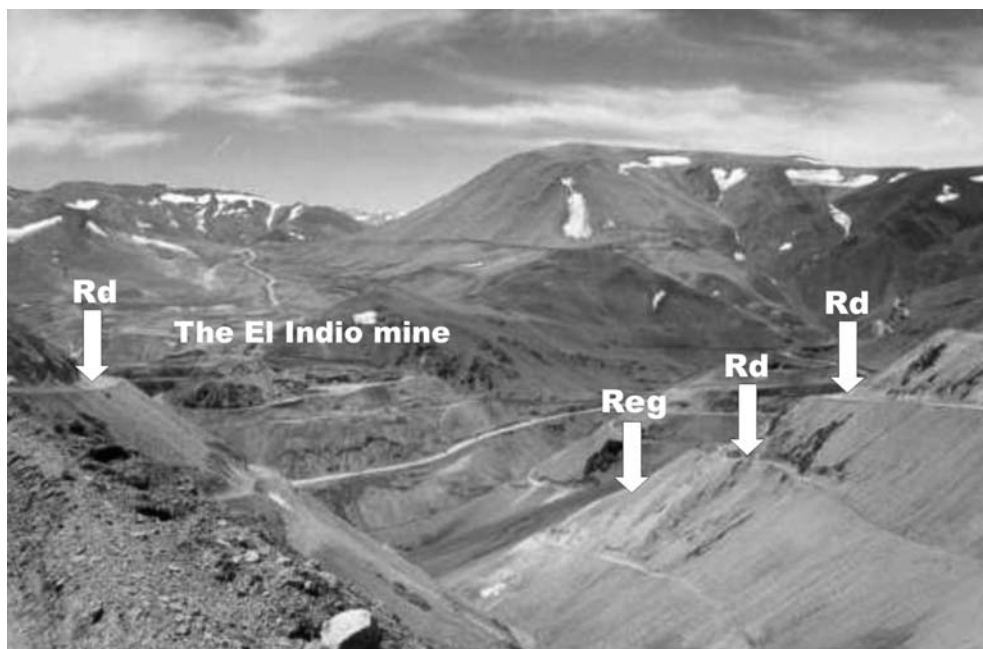


Fig. 3 The El Indio mine, note the smooth slopes formed by a fine grained regolith (Reg) usually rich in As and metals; the regolith has been cut by important road (Rd) building and

exploration works. During the initial works of exploration, As concentrations exceeding 3500 mg kg^{-1} were detected in the area (soil geochemistry) (Siddeley & Araneda, 1986)

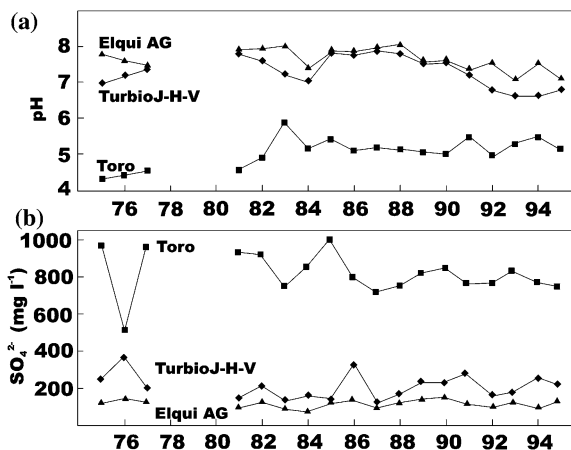


Fig. 4 (a) pH annual average (rolling means) in the waters of the rivers Toro, Turbio, Elqui, and La Laguna, for the period 1975–1995. (b) Sulfate annual average (rolling means) in the waters of the rivers Toro, Turbio, Elqui, and La Laguna, for the period 1975–1995. AG: Algarrobal; H: Huanta; J: Juntas; V: Varillar. The rolling means were calculated in the following way: given the sequence of data, we defined a new n -moving sequence, by taking the average (rolling mean) of subsequences of n terms. Thus, the plot is a filtered curve

both the Turbio and the Elqui rivers have much larger pH values than those of the Toro (Fig. 4a). Same as in the case of metals, the latter can be explained in terms

of the dilution induced by the arrival of water from the tributaries. On the other hand, the SO_4^{2-} contents in the river waters (Fig. 4b) generally match in a reverse way the pH values. For example, the 1981–1995 river Toro SO_4^{2-} contents show a tendency towards lower values, whereas in 1988 sulfate increased in the river Turbio. Same as in the pH case, we can explain this behavior in terms of the initiation of mining works at Carmen.

Given the health concerns regarding As contents in river waters that are used for irrigation purposes (the water for human use is previously treated) in the region, we studied the problem under a wide time perspective (1975–1995). The log-probability plots for the main rivers show remarkable results (Fig. 5). As one may expect, the potential health hazards systematically diminish from the Toro to the Elqui river, although the latter present a significant number of data which fall within the field of contaminated waters for irrigation purposes ($\text{As} > 0.1 \text{ mg l}^{-1}$; as defined by the Chilean law NCh N°1333 Of87) (Table 3). Given the importance of the agricultural sector in the Elqui valley (e.g., papaws, kiwis, custard apples, avocados, olives, sweet grapes; among others), this finding should be a matter of major concern.

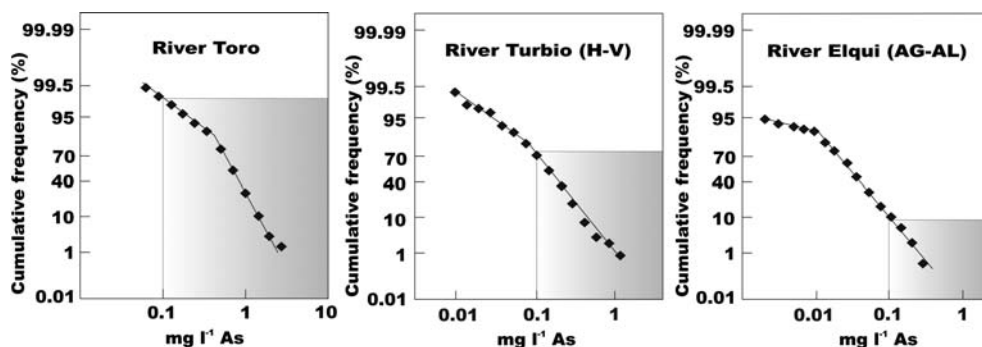


Fig. 5 Log-probability data distribution for arsenic in the rivers Toro ($n=188$), Turbio (Huanta-Varillar; $n=283$), and Elqui (Algarrobal–Almendral; $n=243$). Period: 1975–1995.

Shaded areas: concentration above the maximum level of As in waters (0.1 mg l^{-1}) used for irrigation purposes (Chilean law NCh No 1333 Of87)

Table 3 Maximum contaminant levels (MCLs) for As and Cu, and world and local mean concentrations in river waters for As, Cu, and Fe

As (mg l^{-1})	Cu (mg l^{-1})	Fe (mg l^{-1})
MCLs for drinking water (USEPA, 2004)		
0.01	1.3	
MCLs for irrigation water (Chilean law NCh N°1333 Of87)		
0.1	5.6	5.0
World average for river waters (Gaillardet et al., 2004)		
0.0006	0.0015	0.066
Northern Chile (Smedley & Kinniburgh, 2002)		
0.1–1.0		
River Loa (northern Chile), lower-middle course (Romero et al., 2003)		
1.1–10		
Elqui watershed (Dittmar, 2004)		
<0.01–0.09	<0.06–5.91	0.19–8.77

Factors that influence element behavior in the Elqui system

We will now examine the geochemical behavior of As in the Elqui watershed, and the possible pathways for the introduction of this element into the rivers. Arsenic is mobile under a wide range of pH and Eh, as either oxyanions of arsenite (As^{+3}) or arsenate (As^{+5}). If conditions are oxidizing (as in the Elqui basin; Oyarzun et al., 2004), arsenate species (e.g. HAsO_4^{2-}) dominate over those of arsenite (e.g. H_2AsO_3^-). The source areas of arsenic are varied, although the main ones are related to geothermal fields and mineral deposits (natural sources) and mining operations (anthropogenic sources). Not only arsenic minerals such as enargite (Cu_3AsS_4), or tennantite [$(\text{Cu,Fe})_{12}\text{As}_4\text{S}_{13}$], are to be regarded as

potential sources of arsenic, because pyrite (FeS_2) can be also extremely rich in this element (up to 7.7%) (Smedley & Kinniburgh, 2002). Although the igneous rocks are generally poor in arsenic, the volcanic ash deposits (tuffs) may be implied in the generation of high-As waters (Smedley, Nicolli, Macdonald, Barros, & Tullio, 2002). These features are particularly relevant to the Elqui watershed case because of the presence of important units of Miocene pyroclastic (ash type) deposits. Additionally, the whole high-altitude belt of alteration zones was the result of large-scale, time-persistent geothermal activity during the Miocene. Furthermore, arsenic is a typical element associated with epithermal processes of the acid-sulfate type (high-sulfidation systems), and occurs in mineral assemblages of the type enargite-pyrite (Heald, Foley, & Hayba, 1987). This is particularly relevant to the case of the epithermal deposits of El Indio, which hosts two types of veins (Siddeley & Araneda, 1986): (1) massive sulfides (enargite-pyrite); and (2) quartz-gold. The massive sulfide veins (before mining) were up to 200 m long and 0.5–12 m thick, and had grades of 6–12% Cu, 4–10 gt^{-1} Au, 60–120 gt^{-1} Ag. The quartz-gold veins (before mining) were up to 200 m long and 0.5–6 m thick. However, the latter veins were not devoid of arsenic and sulfur, which reached mean values of 1.7% As and 7.4% S (Siddeley & Araneda, 1986).

The oxidation and leaching of arsenic ores in the superficial environment of pyrite-enargite veins lead to formation of H_3AsO_4 : $\text{Cu}_3\text{AsS}_4 + 5.5 \text{Fe}_2(\text{SO}_4)_3 + 4 \text{H}_2\text{O} \rightarrow 3 \text{CuSO}_4 + 11 \text{FeSO}_4 + 4 \text{S} + \text{H}_3\text{AsO}_4 + 2.5 \text{H}_2\text{SO}_4$ (Escobar, Huenupi, & Wiertz, 1997). However, as pH increases, H_3AsO_4 becomes unstable, and

the dominant arsenic species is H_2AsO_4^- ($\text{pH} > 2$; Smedley & Kinniburgh, 2002). On the other hand, the oxidation process of pyrite is a net producer of goethite: $4\text{FeS}_2 + 10\text{H}_2\text{O} + 15\text{O}_2 \rightarrow 4\text{FeO}(\text{OH}) + 16\text{H}^+ + 8\text{SO}_4^{2-}$. Colloidal goethite has a net positive charge (e.g. Seaman, Bertsch, & Strom, 1997) in acid media, which binds negatively charged arsenic complex ions by adsorption. These complex ions may remain strongly bound to goethite up to higher pHs of 8.0–8.5 (Davis & Kent, 1990; Smedley & Kinniburgh, 2002; Smith, 1999). Desorption of arsenic from goethite may occur by competition between negative charges for the positive colloid, a reduction of the iron oxide mineral phase (Meng, Korfiatis, Bang, & Bang, 2002), or high pH values (> 8.5). Given the Eh-pH conditions of the superficial environment of the supergene alteration zones (oxidation environment; As source area), we may rule out the second and third possibility. The As complex ions which are not adsorbed by goethite will migrate in solution either as H_2AsO_4^- at $\text{pH} = 2-7$ or as HAsO_4^{2-} at $\text{pH} \geq 7$ (Smedley & Kinniburgh, 2002). Given the pH values measured in the rivers (Fig. 4a), we expect both aqueous species to be present, H_2AsO_4^- in the river Toro, and HAsO_4^{2-} in the rivers Turbio and Elqui. However, the notorious decrease in pH in the river Turbio from 1988 onwards, could have favored the presence of H_2AsO_4^- as the dominant species.

Given the mountainous landscape, the high-altitude character of the tributary rivers of the study region, and the periodic development of high-intensity rain storms, we may assume that the As-, goethite-rich regolith in the alteration zones is easily washed down to the rivers, and transported as particles of different sizes. However, a comparison of rainy and dry years (Fig. 2a, c–f) shows surprising results (Fig. 6). We do not detect significant variations in metal contents, which may be explained in the following way: increased rains would wash out metals more easily, however, the increased river flow would also result in higher rates of dilution. On the other hand, less rain means diminished erosion, and therefore lesser metal leaching. The analysis of seasonal variations in the Toro and Turbio rivers may provide some useful insights into this issue (Fig. 7). Arsenic behave in different ways: in the river Turbio increases its concentration from May to September when the river flow is low, however, along the Toro

the case is different, with many oscillations and no clear pattern (although the largest concentrations are reached during high river flow: December–January). A similar behavior is shown by copper. In the case of the river Turbio one may conclude that element concentration largely depends on river flow, however, this can hardly be applied to the most contaminated studied river: the Toro. Although some high As and Cu concentrations are recorded during the austral winter months (low river flow), the behavior of both elements along the Toro is essentially erratic. This may indicate that other factors strongly influence element concentration, e.g., mining activities, whose effects should be far more important along the Toro than in the Turbio. Iron is an entirely different matter. For example, Fe concentration in the river Toro follows a pattern similar to that of the flow, i.e., the lowest the flow, the smallest the concentration of Fe. This can be explained in terms of increasing Fe precipitation (as oxyhydroxides) when river flow decreases (e.g., Olías, Nieto, Sarmiento, Cerón, & Cánovas, 2004). This idea is further supported by

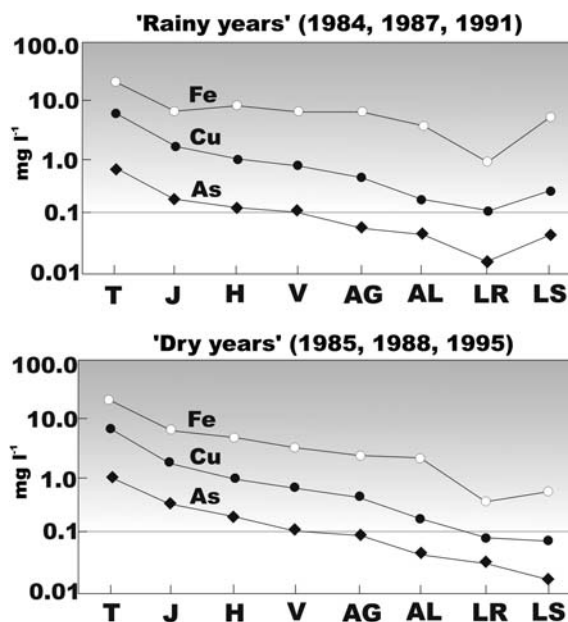


Fig. 6 As–Cu–Fe concentrations during rainy and dry years, in the different sampling stations for the period 1974–1995. AL: Almendral; AG: Algarrobal; H: Huanta; J: Juntas; LR: Las Rojas; LS: La Serena; T: Toro; V: Varillar. Shaded areas: concentration above the maximum level for As in waters (0.1 mg l^{-1}) used for irrigation purposes (Chilean law NCh No 1333 Of87)

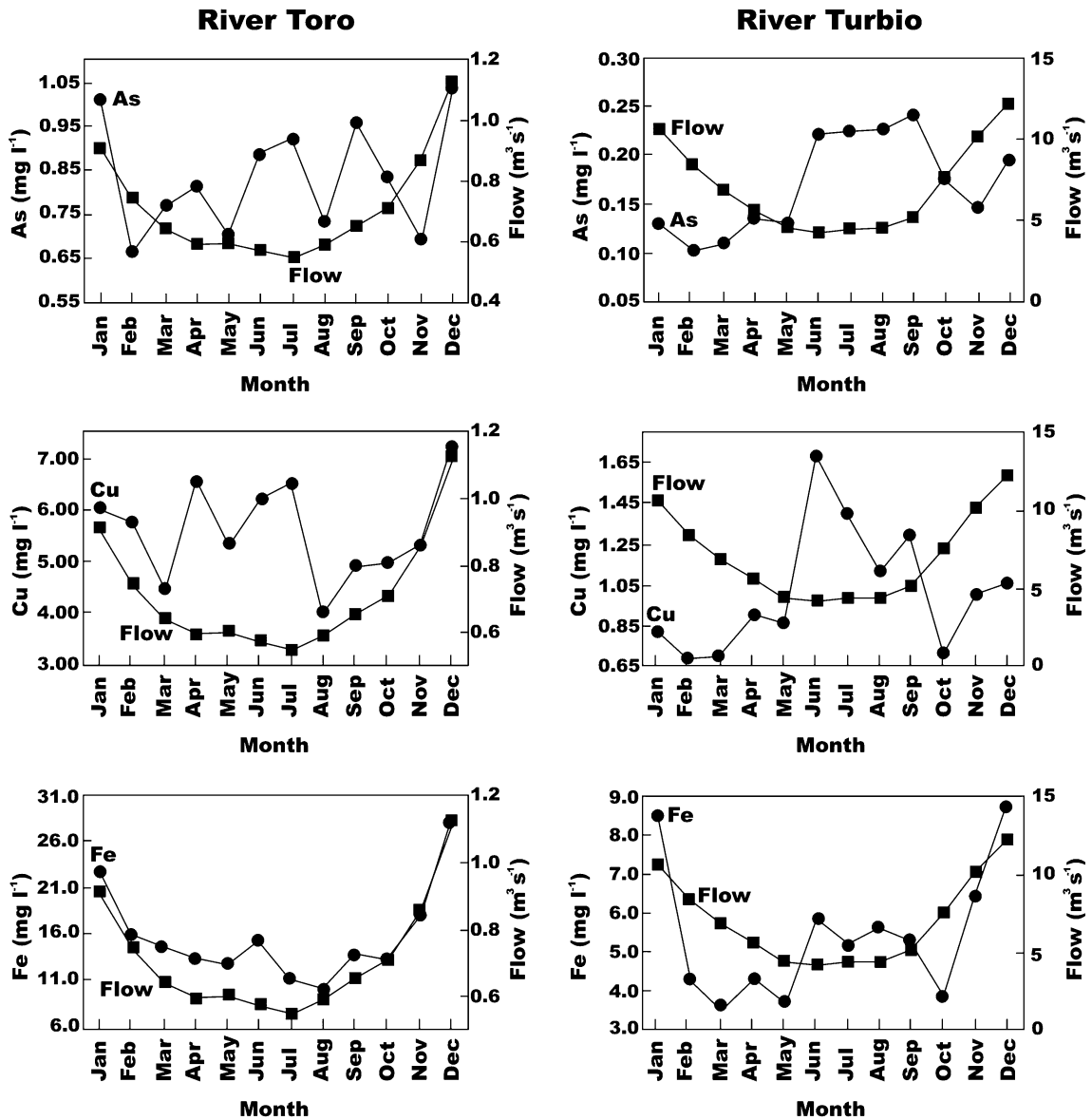


Fig. 7 Seasonal variation in As, Cu, and Fe concentration, and river flow in the Toro and Turbio. Mean monthly concentrations

several lines of evidence suggesting that iron oxyhydroxide precipitation takes place mainly in the autumn and winter months (Poage, Sjostrom, Goldberg, Chamberlain, & Furniss, 2000). In the river Turbio the case is different. Although Fe concentration increases during the austral winter months (June–August), the highest concentrations are found during December–January, which may indicate that Fe concentration is being ruled first by increasing precipitation of oxyhydroxides (January–May), followed by a rapid decrease. We suggest that the latter

may be a consequence of decreasing levels of dissolved oxygen during low river flow (e.g., Jiann, Wen, & Santschi, 2005), which in turn would inhibit oxyhydroxides precipitation.

Removal of As in the Elqui system: the role of goethite

Although stormy rainy episodes lead to the rapid and strong erosion of the As rich regolith, the sampling procedure (involving the filtering of the water) results

in rejection of the particulate matter, and therefore this arsenic cannot be easily detected. This idea is supported by the distribution of arsenic in fluvial sediments along the Elqui system. Sediment samples collected downstream the Puclaro Dam (built between 1996 and 1999; total capacity: 200 Mm³) have four times less arsenic than those taken immediately upstream (Oyarzun et al., 2004), thus suggesting that arsenic is strongly bound to the sediment fraction (retained by the dam). While reducing environments lead to desorption of arsenic from iron oxide minerals (Smedley & Kinniburgh, 2002), the Elqui watershed provides oxidizing conditions (Oyarzun et al., 2004) allowing the existence of goethite (FeOOH) that binds the arsenic species. In turn this mineral phase is incorporated to the sediments, thus removing part of the arsenic dissolved in the waters. In this respect it may be useful to analyze the time distribution of Fe values. There is a remarkable increase in Fe from 1987 to 1988 onwards in the rivers Toro and Turbio (Fig. 2c, d). Part of the increase in the latter can be explained in terms of the rise of iron in the river La Laguna (Fig. 2f), although a better explanation can be found in the lowering of pH (Fig. 4a): the lower the pH the higher the solubility of iron. As shown in Fig. 4a, the 1987–1988 lowering of pH in the Elqui is not as important as in the river Turbio, and conspicuously, although oscillating, there is a long range trend (1982–1994) towards lower Fe contents (Fig. 2e). Given that Fe has an opposite behavior in the Toro and Elqui rivers during the same time span, we may conclude that part of the iron in the Elqui has precipitated as hydrous oxide species (e.g. Oyarzun et al., 2004). Dittmar (2004) indicates that pH buffered waters in the upper river system causes collapse of iron hydroxide colloids and coprecipitation of heavy metals. However, as shown in Fig. 2c, d iron doubled its concentration in the rivers Toro and Turbio, which means that an important part of the metal remained in solution. In any case, there is evidence indicating that metals do get absorbed to the iron hydroxide phase, and that the As contents in the sediment fraction diminish from the HAFS to the Elqui, from initial values of 320 mg kg⁻¹ As (Toro) to 108 mg kg⁻¹ As (Elqui) (Oyarzun et al., 2004). Additionally, the study of the Turbio Early Holocene lacustrine sedimentary sequence (with contents of 119–2344 mg kg⁻¹ As) shows remarkable results

regarding the relationships between As and iron oxide phases. In this respect there is clear evidence of As bound to the goethite phase. That fraction presents typical contents of: As (1.53–2.35%), Cu (traces–0.89%), Zn (traces–0.44%), Fe (35.2–52.2%), with very low sulfur (1.45–4.36%), which suggests that the oxide phase derived from the almost total oxidation of sulfide minerals (Oyarzun et al., 2004). We may interpret the decrease in Fe in the Elqui river (Fig. 2e) as the result of increasing rates of iron oxide precipitation. However, given that As has systematically increased in the Elqui during the 1982–1995 period, we may infer that As is not being bound to goethite. This could be the result of the neutral to slightly alkaline character of these waters (Fig. 4a). Under these conditions goethite does not behave as a positive colloid, and therefore the negatively charged arsenic oxyanions cannot be captured.

Short versus long-lived As contamination in the Elqui system: final considerations

As shown by Fig. 2b, c there is clear evidence indicating that mining activities in the high altitude realm of the Elqui system has disrupted the normal geochemical behavior of As and Cu–Fe. The river La Laguna case (the 1988–1992 Carmen episode) may serve as an example of how disruptive can be mining activities regarding the introduction of metals into the river system (Fig. 2f). Furthermore, all the As values are above the 1975–1977 baseline. However, as shown by Oyarzun et al. (2004), there is also evidence of long-lived transport of As and Cu towards the Turbio river. The sequence of lacustrine sediments (*c.* 10,000 years old) perched along the walls of the river contains an average of 749 mg kg⁻¹ As and 697 mg kg⁻¹ Cu. Given that the sequence is well above the present bottom of the valley, these values cannot be derived from present contamination along the river. Once erosion starts, the unroofing of a mineral deposit may lead to the massive and sustained leaching of metals, and therefore, to long-lived ‘natural contamination’ of rivers. The longer the process, the greater the effect. Therefore, we suggest that Elqui system has been subjected to both, natural (long-lived) and industrially induced contamination processes, and as such, the cease of operations at El Indio will diminish, but not end, the introduction of

As and heavy metals to the river system. In the best case, the values will return to the 1975–1977 As baseline (Fig. 2c–f), which in any case, is well above the world average for river waters (Table 3).

Conclusions

The Elqui watershed represents a highly contaminated river system in terms of As, Cu, and Fe. The concentrations of these elements in the waters exceed by up to three orders of magnitude those of the world average for river waters. The reasons for these concentrations are to be found in: (1) the regional geology and hydrothermal processes that developed in this realm during Miocene time; (2) the subsequent unroofing-erosion of the ores that took place during the Holocene; and (3) the important mining activities that took place at the El Indio mine. Arsenic is an element can be closely associated to hydrothermal systems of the acid–sulfate type leading to formation of precious metals epithermal deposits. This is the case of El Indio, which hosted (before production) large veins of massive sulfides including the important presence of the mineral enargite (Cu_3AsS_4), which different to the case of simple gold epithermal deposits, made also possible the extraction of Cu and As. The continuous natural erosion of these deposits and their host rocks (also rich in As and Cu) for at least 10,000 years led to important metal dispersion along the river system. As shown by the 1975–1977 period (our pre mining baseline), the river Toro already had very high As concentrations (in the range of $0.36\text{--}0.52\text{ mg l}^{-1}$), and the same applies to the rivers Turbio and Elqui. However, the initiation of full scale mining at El Indio (1980 onwards) led to an increase of these concentrations. For example, the Toro river reached a mean concentration of 1.51 mg l^{-1} in the year 1995. Taking all this into account, we suggest that the end of mining at El Indio will diminish, but not end, the introduction of As and heavy metals to the river system, which in the best case should return to the high 1975–1977 baseline.

Acknowledgements The authors are much indebted to the Dirección General de Aguas de Chile (CWA) for allowing the use of their 1975–1995 data files. We also want to thank the Regional Government (Coquimbo region), the Research Office of the University of La Serena, the Spanish Agency for

International Cooperation (AECI), and the Bureau of International Cooperation of the University of Castilla La Mancha for their encouragement and continuous support during this investigation. Additional funding was obtained from Grant 910386 (Universidad Complutense; Grupos de Investigación). The manuscript benefited from the comments of two anonymous reviewers.

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