Journal of Hazardous Materials 181 (2010) 747–754

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Heavy metals in northern Chilean rivers: Spatial variation and temporal trends

Jaime Pizarro*, Pablo M. Vergara, José A. Rodríguez, Alejandra M. Valenzuela

Departamento de Ingeniería Geográfica, Facultad de Ingeniería, Universidad de Santiago de Chile, Av. Lib. B. O'Higgins 3363, Santiago, Chile

ARTICLE INFO

Article history:
Received 13 January 2010
Received in revised form 14 May 2010
Accepted 17 May 2010
Available online 24 May 2010

Keywords:
Heavy metals
Chilean rivers
Annual trends
Mining

ABSTRACT

Rivers of central-northern Chile are exposed to pollution from different sources, including mining activities, natural orogenic process, volcanic activity, and geology. In order to determine the contribution of mining to river pollution, the spatio-temporal dynamics of chemical species dissolved in 12 rivers of central-northern Chile was assessed. Of all the rivers studied, the Elqui showed the highest historical mean concentrations of As, Cu and Pb. The Aconcagua had the highest concentration of Hg and a large Cr concentration, while the Rapel showed elevated concentrations of Cu and Mo. The Elqui and the Aconcagua were clustered as distinct groups by a cluster analysis based on two independent principal components. Hierarchical Bayesian models showed annual trends but no seasonal effects in heavy metal concentrations. As and Cu in the Elqui had positive annual slopes. Sulphate concentration exceeded 100 mg L^{-1} in nine rivers, and in seven of them it had positive annual slopes. Our findings suggest that mining pollution is the main process contributing to this increasing annual trend in As, Cu and SO_4^{2-}. Therefore, in order to improve the water quality of these rivers it is necessary to identify the main sources of heavy metals associated with mining activities.

1. Introduction

Rivers play an important role in population development, supplying water for humans, agriculture, and industrial consumption. Anthropogenic activities such as mining, agriculture, residential wastes, and industrial wastes systematically discharge dissolved compounds and suspended matter into the rivers, decreasing water quality significantly [1–5]. Polluted inflows of rivers can have severe impact on human health as well as on terrestrial and aquatic ecosystems [6], and it is therefore necessary to assess their spatio-temporal behaviour in order to develop control and management strategies for pollution control.

Water pollution from mining activities is a concern for several rivers around the world [7,8]. Mining wastes are important sources of chemical species, such as As, Cu, Cr, Hg, SO_4^{2-}, Cd, Mo and Pb [9–16]. As a result of the continuous emission of these chemical species into the rivers, the concentration levels of such species could exceed critical threshold values for human and ecosystem health [3]. Therefore, assessing the impact of mining on water pollution is an important goal to conserve ecosystem processes and supply water for human consume.

In Chile there is increasing interest in determining how human activities affect the concentration of heavy metals (e.g. Cu, Zn, Cd, Hg), metalloids (As), and other polluting compounds responsible for decreased water quality [17–20]. Human activities associated with mining industries, such as metal-rich mine tailing and mineral deposits, are important sources of polluting compounds that decrease water quality in several river basins in the northern-central region of Chile [18,20–22].

In Chile and other regions of the world the lack of historical data on heavy metals dissolved in water hampers our ability to test properly the effects of mining on heavy metal concentration [23]. Mining discharges into rivers in Chile can have a detrimental effect on natural aquatic ecosystems, but natural orogenic process, volcanic activity, geology, and an arid climatic regimen can also explain the high heavy metal concentration in Chilean freshwater systems [19,24,25]. Although it is difficult to separate natural from anthropogenic effects on heavy metal concentration, determining whether heavy metal concentrations have increased over time may give us insights into the effect of mining pollution.

Current studies of Chilean rivers have revealed an increase in the concentrations of heavy metals during the last two decades; Oyarzún [21] detected a positive temporal trend in As concentration in the Elqui river, which may be associated with the beginning of activities of a large gold mine in the 1980s. Moreover, other studies have suggested that mining discharges into important Chilean rivers (e.g., Elqui, Limarí, Choapa, and Maipo), can be important to account for high concentrations of Cu, Zn, Cd, Fe, Mn, and Pb [19,25,26].

A large number of mines, mainly gold and copper, and a small number of iron and manganese mines, are found in the northern Chilean basins (Table 1). Chilean mining in the central-northern

* Corresponding author. Tel.: +56 2 7182226.
E-mail address: jaime.pizarro@usach.cl (J. Pizarro).

0304-3894/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2010.05.076

Table 1
Current number of mines, classified according to their annual production (large mines: >3 million ton $year^{-1}$, medium mines: 100 thousand >3 million ton $year^{-1}$, and small mines: <100 thousand ton $year^{-1}$) and ore type in the main rivers of central-northern Chile.

River	Area (km^2)	Mines by production size				Type of mine			
		Large mines	Medium mines	Small mines	Total	Copper	Gold	Copper–gold	Other
Endorreica	15,619	1	0	3	4	0	3	0	1
Copiapó	18,400	6	15	73	94	68	26	0	0
Huasco	9850	1	2	19	22	16	6	0	0
Los Choros	3838	0	0	31	31	8	16	6	1
Elqui	9826	10	5	93	108	32	58	10	8
Limarí	11,800	2	3	86	91	55	20	12	4
Choapa	8124	2	1	95	98	25	30	43	0
Petorca	1986	1	4	43	48	27	20	1	0
Ligua	1982	1	18	53	72	58	11	3	0
Aconcagua	7340	9	0	51	60	53	6	0	0
Maipo	15,304	3	4	49	56	31	13	10	1
Rapel	13,695	3	2	61	66	4	62	0	2
Total	117,764	39	54	657	750	377	271	85	17

region, however, is not regularly distributed across such basins (e.g., Elqui and Huasco concentrate 108 and 22 mines respectively; Table 1). Therefore, rivers with more mining activities are expected to have high concentrations of heavy metals. With the purpose of contributing to the understanding of the dynamics of heavy metal concentrations in northern Chilean rivers, this study aimed at determining annual and seasonal trends in heavy metals.

2. Materials and methods

2.1. Study site

Twelve important rivers of central-northern Chile (from 25° 17′ to 35° 01′ S lat, Fig. 1) were studied. The climate of this area is semi-desertic, characterized by a low precipitation regime (mean annual precipitation <200 mm). However, all the rivers are located over an altitudinal climate gradient, with their upper sections (>3000 m.a.s.l.) influenced by a high-Andean climate characterized by low minimum temperatures (<−10 °C), local snow precipitations during winter, and an annual average rainfall of ca. 100 mm. In addition, the northernmost basins (Endorreicas to Choapa) receive abundant rainfall during the summer, a climate phenomenon locally called "Bolivian winter", which can locally increase the average annual rainfall to ca. 300 mm (Fig. 1).

2.2. Study areas

A sampling database from the National River Monitoring Network of the Ministry of Public Works of Chile was used (Dirección General de Aguas, DGA). The DGA's sampling stations are systematically distributed along the main tributaries of each river basin (i.e., "sub-basins"), covering from the river head to the river mouth (Fig. 1, Table 2). Thus, the DGA's data set can be considered a random sample of all river network.

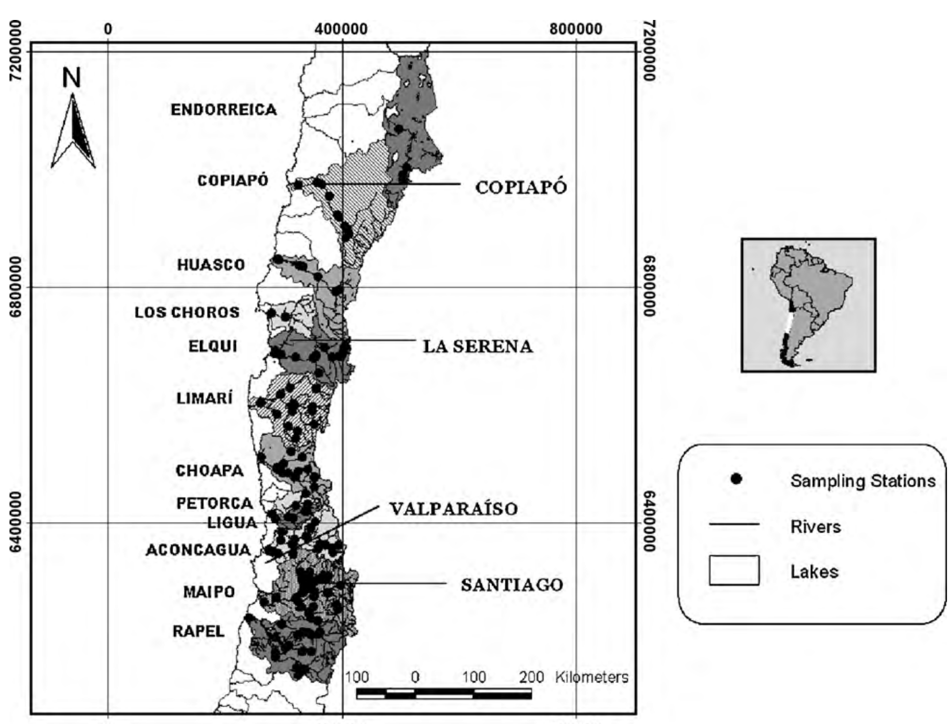

Fig. 1. Map of the river basins studied in the central-northern Chilean region showing the main cities in that region (Copiapo, La Serena, Valparaiso and Santiago).

Table 2
Number of sampling stations, sampling data records, sampled years, total number of sampling years, and mean water flows (and their standard errors) for the nine rivers analyzed in this study.

River	Sampling stations	Data records	Sampled years	Number of years	Waterflow ($m^3 s^{-1}$)	SE
Endorreicas	4	727	1980–1983, 1985–2008	28	0.17	0.01
Copiapó	10	3154	1980–2007	28	1.51	0.09
Huasco	8	2930	1980–1981, 1984–1986, 1990–2007	23	4.81	0.34
Los Choros	2	598	1998–2007	10	0.01	0.01
Elqui	20	10,510	1981–2007	27	5.48	0.18
Limarí	15	4945	1980–1990, 1992–2007	27	4.65	0.30
Choapa	14	4356	1980–1990, 1992–2007	27	6.76	0.66
Petorca	4	1509	1986–2007	22	1.91	0.20
Ligua	5	1525	1980–2007	28	2.52	0.29
Aconcagua	19	7226	1980–2007	28	11.84	0.73
Maipo	42	13,378	1980–2008	29	34.91	0.75
Rapel	18	6302	1980–2007	28	29.82	0.95

2.3. Sampling

At each sampling station, surface water was collected seasonally. The water samples were kept in 0.5 L polypropylene sampling bottles at 4 °C and analyzed within 48 h. The chemical species were determined using SMEWW methodology [27]. Cadmium, copper, chromium, lead, and molybdenum were measured by atomic absorption spectroscopy, with detection limits of 0.01 mg L^{-1} for Cd, Cu and Cr, and 0.05 mg L^{-1} for Pb and Mo; arsenic and mercury were determined by hydride generation atomic absorption spectrophotometry and cold-vapour atomic absorption spectrometry (CV-AAS), with detection limits of 0.001 mg L^{-1} in both cases. Sulphate was determined by the turbidimetric method ($BaCl_2$) with a detection limit of 0.001 mg L^{-1}. Concentration data below the detection limits were not considered in this study.

2.4. Statistical analysis

The "historical" means of chemical species concentration of each river, based on pooled samples in the study period was estimated. Principal component analysis (PCA) and multivariate cluster analysis (CA) was used to determine differences in normalized chemical species concentrations between rivers. PCA allowed the reduction of several chemical species variables to a small set of uncorrelated factors, and cluster analysis was used to classify rivers into groups based on scores of these factors.

The standardized historical means of five chemical species, As, Cu, Cr, Hg, and SO_4^{2-}, were used for PCA. Factor loading and component matrices of the latter variables were defined. Following Liu et al. [28], factor loadings were classified as "strong," "moderate," and "weak" if the loading values were >0.75, 0.75–0.50, and 0.50–0.30, respectively. Factors with an eigenvalue greater than unity were considered significant. Based on each significant principal factor obtained by PCA, CA was performed by means of Ward's method using Euclidean distance as a measure of similarity. A similarity threshold of 60% was used as a criterion for defining statistically significant clusters.

Hierarchical Bayesian models (HBM) were used to assess annual and seasonal trends in the concentrations of chemical species. HBM is a powerful statistical technique that incorporates stochastic effects at multiple levels in a manner similar to frequentist random-effects models, but allowing parameter variation across several related spatial or temporal replicates [29,30]. Parameter estimation is achieved using Markov Chain Monte Carlo (MCMC) and the Metropolis Hastings algorithm [29]. This approach implies that parameters are considered as random variables because they are generated from MCMC that converges to the posterior distribution of these parameters [29–31].

HBMs were developed using As, Cu, and SO_4^{2-} concentrations as dependent variables because only for these three chemical species it was possible to obtain reliable estimations of MCMC coefficients (see below). In these models a hierarchical nested error structure was included to control for random spatial variation associated with basin level, sub-basin level, and sampling station [5]. The season, year, and water flow were added sequentially as independent (fixed effect) variables into the model and model performance was compared. Water flow was standardized at the river level to control for differences in water flow between rivers [5]. Previously, we determined that the standardized water flow per basin was not correlated with the year (i.e., there were no trends in water flow; all $P > 0.08$), thereby avoiding multi-collinearity problems in models. The Deviance Information Criterion (DIC) was used as a model selection criterion penalizing model complexity, which is similar to the Akaike information criterion [29]. Models were ranked from most to least supported given the data based on ΔDIC (the difference in DICc between the model with the smallest DIC value and the current model). If necessary, concentrations were transformed to minimize deviations from normality.

In order to estimate model coefficients, four chains were initialized with different points in parameter space. A burn-in period of 10,000 iterations and a further 30,000 iterations were used to get low Monte Carlo standard errors of the mean (MC error) and low autocorrelation levels. The sampled values for each MCMC coefficient were visually monitored for convergence. Annual MCMC coefficients (i.e., annual "slopes") were estimated separately for each river, except for rivers where sample size was insufficient to detect an annual trend ($n < 100$). From the posterior distribution of sampled MCMC coefficients the mean and the Bayesian 95% credible intervals (i.e., the 2.5th and 97.5th percentile) of coefficients were computed and tested in order to determine if the coefficients were "significantly" different from 0. The R package R2WinBUGS was used to write a WinBUGS 1.4 script, call the model, and save the simulations [32].

3. Results

3.1. Chemical species concentration

The historical averages of chemical species concentrations were different between the rivers and for several rivers they exceed the Chilean Water Irrigation Guidelines (CWIG). For As, the Elqui had the highest mean concentration, and the Los Choros and Limarí had the lowest mean value (ca. 284 times lower), while seven rivers exceed the CWIG value (Table 3). For Cd, the Huasco had the highest mean concentration, while the Endorreicas had the lowest mean value (ca. 3.6 times higher, Table 3). However, Cd averages were estimated using small samples (except for the Elqui), and in several rivers there were no concentration data above the detection limit, while eight rivers exceeded the CWIG value (Table 3). The Elqui, followed in decreasing order by the Rapel, Endorreicas, and Maipo,

Table 3
Mean concentrations of chemical species in 12 rivers of central-northern Chile sampled between 1987 and 2008. Chilean water irrigation guidelines (Ministry of Economy, Instituto Nacional de Estadísticas, INE) are shown in brackets.

River basins	As ($\mu g L^{-1}$) (100)		Cu ($\mu g L^{-1}$) (200)		Cr ($\mu g L^{-1}$) (100)		Hg ($\mu g L^{-1}$) (1)	
	Mean ± SE	n	Mean ± SE	n	Mean ± SE	n	Mean ± SE	n
Endorreicas	814 ± 133	110	2440 ± 2152	22	28 ± 8	10	9 ± 3	5
Copiapó	483.6 ± 25.9	468	77 ± 22	13	60 ± 0	2	148 ± 37	4
Huasco	10 ± 1	318	123 ± 79	195	31 ± 3	41	6 ± 1	20
Los Choros	175.6 ± 11.6	53	NA		60 ± 0	1	817 ± 717	3
Elqui	1705 ± 175	2627	6082 ± 321	2345	26 ± 1	142	3 ± 0	52
Limarí	6 ± 0	529	41 ± 4	230	30 ± 6	7	3 ± 0	20
Choapa	14 ± 4	554	78 ± 11	299	25 ± 2	48	4 ± 1	27
Petorca	182 ± 85	126	43 ± 4	68	54 ± 13	17	3 ± 0	13
Ligua	54.4 ± 2.3	272	NA		68 ± 5	4	NA	
Aconcagua	132 ± 26	910	789 ± 81	908	25 ± 1	40	87 ± 29	62
Maipo	12 ± 0	1608	1293 ± 229	1309	55 ± 6	241	9 ± 2	126
Rapel	119.3 ± 5.2	851	45 ± 15	2	215 ± 32	86	281 ± 110	11

River basins	SO_4^{2-} ($mg L^{-1}$) (250)		Cd ($\mu g L^{-1}$) (10)		Mo ($\mu g L^{-1}$) (10)		Pb ($\mu g L^{-1}$) (5000)	
	Mean ± SE	n	Mean ± SE	n	Mean ± SE	n	Mean ± SE	n
Endorreicas	236.3 ± 7.8	113	26 ± 4	3	60 ± 0	2	NA	
Copiapó	483.60 ± 5.90	468	77 ± 22	13	60 ± 0	2	148 ± 37	4
Huasco	360.24 ± 18.88	432	93 ± 27	14	60 ± 0	2	292 ± 222	6
Los Choros	175.66 ± 11.65		NA		60 ± 0	1	817 ± 717	3
Elqui	445.67 ± 11.22	1376	28 ± 2	156	70 ± 3	26	147 ± 23	42
Limarí	77.11 ± 2.55	728	35 ± 15	4	60 ± 0	1	60 ± 0	1
Choapa	110.55 ± 5.00	697	43 ± 23	3	138 ± 21	17	63 ± 3	3
Petorca	52.77 ± 1.90	262	NA		63 ± 3	3	NA	
Ligua	54.35 ± 2.31	272	NA		68 ± 5	4	NA	
Aconcagua	115.11 ± 1.88	1152	NA		175 ± 81	35	80 ± 14	4
Maipo	215.62 ± 3.33	2047	35 ± 15	2	463 ± 113	37	167 ± 24	43
Rapel	119.30 ± 5.22	851	45 ± 15	2	215 ± 32	86	281 ± 110	11

NA, not available.

had the highest Cu concentration, with only four rivers exceeding the CWIG value, while the other rivers had concentrations lower than 1 $mg L^{-1}$ (Table 3). The historical means of Cr were relatively similar in all the rivers (ranging between 0.025 and 0.055 $mg L^{-1}$), with the Petorca and Maipo having the highest Cr concentration, while only two rivers exceeded the CWIG value (Table 3). Except for the Aconcagua, which had a mean concentration of 0.087 $mg L^{-1}$, the historical means for Hg were relatively similar in all the rivers, ranging between 0.002 (Los Choros) and 0.009 (Maipo and Endorreicas), while all rivers ($n = 11$) exceeded the CWIG value (Table 3) For sulphate, the mean concentration ranged between 52.7 (Petorca) to 483.6 $mg L^{-1}$ (Copiapó), while the Elqui had 445.7 $mg L^{-1}$ and the Endorreica, Huasco, Los Choros, Choapa, Aconcagua, Maipo, and Rapel had mean concentrations higher than 100 $mg L^{-1}$, but only in four rivers sulphate exceeded the CWIG value (Table 3). Historical means of Mo concentrations were higher in the Maipo, Rapel, Aconcagua and Choapa (>0.1 $mg L^{-1}$); while The Endorreica, Copiapó, Huasco, Ligua, Limarí, Los Choros and Petorca had concentrations of about 0.06 $mg L^{-1}$ and all rivers ($n = 12$) exceeded the CWIG value (Table 3). Finally, the mean Pb concentration was higher in the Los Choros, Huasco, Copiapo, Elqui, Maipo and Rapel (>0.10 $mg L^{-1}$), and the Limarí had the lowest concentration (0.06 $mg L^{-1}$). However, Pb averages were estimated using small samples and in several rivers there were no concentration data above the detection limit, although no rivers exceeded the CWIG value (Table 3).

3.2. Principal components analysis

Mean As, Cu, Cr, Hg and SO_4^{2-} concentrations were grouped into two significant factors (eigenvalues >1) extracted by PCA, which accounted for 67.0% of the total variance (Table 4). The first factor (PC1) accounted for 43.2% of the total variance, with moderate loading on Cu and As (Table 4). The second factor (PC2) accounted for 23.4% of the total variance, with moderate loading on Hg and Cr (Table 4).

Table 4
Summary of factor analysis showing variance explained and component matrices for the means of chemical species in Chilean rivers.

Component	Initial eigenvalues		
	Standard deviation	% variance	Cumulative (%)
1	1.47	43.21	43.21
2	1.08	23.44	66.65
3	0.90	16.21	82.86
4	0.81	13.14	96.00
5	0.45	4.00	100.00

Elements	Component matrix	
	PC1	PC2
As	−0.623	0.050
Cu	−0.595	0.047
Cr	0.170	−0.654
Hg	0.116	0.730
SO_4^{2-}	−0.465	−0.183

Based on the first factor, the 12 rivers were classified into two groups by multivariate cluster analysis (Fig. 2). The first group includes only the Elqui, which showed higher concentrations of Cu and especially As than the second group, which contained the remaining 11 rivers (Table 3; Fig. 2). Based on the second factor, the 12 rivers were classified into two groups by multivariate cluster analysis (Fig. 2). The first group includes only the Aconcagua, which showed higher concentrations of Cu and especially As than the second group, which contained the remaining 11 rivers (Table 3; Fig. 2).

Table 5
MCMC mean coefficients, standard deviations (SD), and Bayesian 95% credible intervals for the annual effects on As, Cu and SO_4^{2-} concentrations in the rivers of central-northern Chile. *P*-Values indicate the probability that the sampled MCMC coefficients values are significantly different from 0 ("significant" slopes are marked in bold). The Deviance Information Criterion (DIC) of each model is shown.

Rivers	Mean	SD	2.5%	97.5%	*P*	*n*
As (DIC = 48214.1)						
Endorreicas	0.0120	0.0158	−0.0196	0.204	0.204	110
Aconcagua	0.008	0.013	−0.018	0.033	0.265	910
Choapa	0.008	0.014	−0.021	0.035	0.185	554
Copiapó	0.008	0.014	−0.023	0.036	0.270	456
Elqui	**0.023**	0.012	0.001	0.048	0.000	2627
Huasco	0.008	0.015	−0.023	0.037	0.273	318
Limarí	0.008	0.014	−0.021	0.034	0.184	529
Maipo	0.006	0.012	−0.019	0.029	0.048	1608
Petorca	0.010	0.016	−0.023	0.042	0.373	126
Rapel	0.007	0.014	−0.022	0.034	0.239	732
Cu (DIC = 45849.4)						
Aconcagua	0.028	0.044	−0.059	0.058	0.258	908
Choapa	−0.047	0.053	−0.155	−0.011	0.288	299
Copiapó	−0.038	0.063	−0.162	0.004	0.269	216
Elqui	**0.526**	0.030	0.466	0.547	0.019	2345
Huasco	−0.039	0.067	−0.168	0.006	0.280	195
Limarí	−0.052	0.058	−0.166	−0.013	0.286	230
Maipo	−0.049	0.029	−0.103	−0.030	0.320	1309
Rapel	**−0.115**	0.038	−0.190	−0.089	0.028	656
SO_4^{2-} (DIC = 102455.0)						
Endorreicas	−0.980	1.102	−3.209	1.004	0.811	113
Aconcagua	**1.444**	0.415	0.605	2.268	0.000	1152
Choapa	**1.344**	0.584	0.187	2.471	0.013	697
Copiapó	**4.872**	0.787	3.350	6.446	0.000	468
Elqui	**3.762**	0.383	3.031	4.511	0.000	1376
Huasco	**1.971**	0.753	0.495	3.437	0.005	432
Ligua	0.779	0.784	−0.759	2.306	0.166	272
Limarí	**1.244**	0.502	0.263	2.223	0.007	728
Maipo	**0.761**	0.348	0.072	1.432	0.015	2047
Petorca	0.547	0.774	−0.975	2.059	0.234	262
Rapel	0.101	0.538	−0.959	1.164	0.428	851

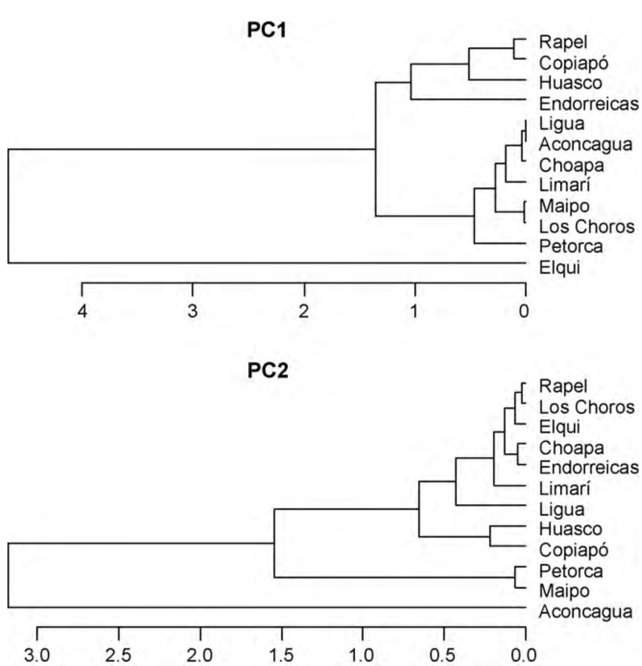

Fig. 2. Dendrograms of Q-hierarchical Cluster Analysis grouping of Chilean rivers based on similarities in PC factors. Above, a dendrogram built using the first factor (PC1), which has moderate loading on Cu and As. Below, a dendrogram built using the second factor (PC2), which has moderate loading on Hg and Cr.

3.3. Trend analysis

HBMs indicated that dissolved chemical species had annual trends but not seasonal variation in some rivers. According to DIC values, the best model explaining As concentration included an annual effect only for the Elqui, with an increase in As concentrations (mean annual slope = 0.023) during the sampling period (Table 5). Other models with seasonal and water flow effects did not fit well with the As data (ΔDIC > 5.6). The best model accounting for Cu concentration included an annual effect for the Elqui, with an increase in Cu concentration during the sampling period (mean annual slope = 0.526), while the Rapel showed a decreasing trend during the same sampling period (mean annual slope = −0.115; Table 5). Other models with seasonal and water flow effects did not fit well with the Cu data (ΔDIC > 4.7). The best model explaining SO_4^{2-} concentration included an annual positive effect for seven rivers: Aconcagua (mean annual slope = 1.444), Choapa (1.344), Copiapó (4.872), Elqui (3.762), Huasco (1.971), Limarí (1.244), and Maipo (0.7607), whereas Endorreicas, Ligua, Petorca, and Rapel did not show significant annual slopes (Table 5). Rivers with higher mean SO_4^{2-} concentrations had larger annual effect coefficients (slopes), as shown by a positive Spearman's correlation coefficient (r = 0.73, P < 0.01, n = 11) between these two variables (Fig. 3).

4. Discussion

The results suggest that chemical species dissolved in the Chilean rivers vary between different rivers as a result of between-basin heterogeneity in anthropogenic activities and natural environmental variability, such as geological characteristics. Furthermore, the concentrations of chemical species have increased steadily over time, probably as a response to dynamic processes

Table 6
Concentration data of chemical constituents in rivers of the world. For comparison purposes, the Food and Agriculture Organization Guidelines for each chemical species are ($mg\,L^{-1}$): As: 0.2; Cu: 0.5; Cr: 1.0; Hg: 0.01; Cd: 0.05; Pb: 0.1.

River (country)	Analytical procedure	As	Cu	Cr	Hg	SO_4^{2-} ($mg\,L^{-1}$)	Cd	Mo	Pb	References
Oitavén (Spain)	Polarography		0.12				0.1		0.21–0.52	[9]
Ulla (Spain)	Polarography		2.50						0.25–4.14	[9]
Mero (Spain)	Polarography		0.41						0.19–1.03	[9]
Anllóns (Spain)	Polarography		0.13–1.02				0.13		0.35–0.68	[9]
Mississippi (USA)	wi	3.00	2.00	0.50	0.10		0.10		0.20	[10]
Rhine (Germany)	wi	13.00	34.00	33.00	0.65		5.50		57.00	[10]
Marne (France)	ICP-MS	0.22–1.06	0.75–3.55				0.012–1.024	0.06–1.31	0.005–2.26	[11]
Seine	ICP-MS	0.36–1.28	0.49–3.47				0.008–2.44	0.05–2.15	0.073–1.021	[11]
Odiel (Spain)	DAPSV, AAS, ICP-MS	2.9–9.3	34.5–57.2				1.3–8.9		3.7–17.8	[12]
Tinto (Spain)	DAPSV, AAS, ICP-MS	3.0–7.5	37.1–72.4				1.3–6.8		3.5–7.4	[12]
Canal Padre Santo (Spain)	DAPSV, AAS, ICP-MS	2.6–6.2	20.9–57.7				0.7–1.7		2.6–6.2	[12]
Nakkavagu stream (India)	ICP-MS	5.5–116.5		4.6–46.8					0.2–13.8	[13]
Nilo (Sudan-Egipt)	wi							0.34–1.74		[14]
Volga (Russia)	wi							0.64		[14]
Amazon (Brasil)	wi							0.42		[14]
Wear (England)	ICP-MS	1.4	2.4; 1.2	0.3; 0.2		99.91		10.3	2.8; 5.4	[15]
Thames (England)	ICP-MS	2.9	4.3; 0.8	0.4; 0.2		85.7		3.2	0.4; 0.7	[15]
Changjiang (China)	Neutron activation**, AAS***, Polarograph*v, cold AASv	1.20	9.60	0.30		19	0.004	1.00	1.46	[8]
Huanghe (China)	Neutron activation**, AAS***, Polarograph*v, cold AASv	2.7	3.29	0.30		109.40	1.17		4.49	[8]
Red river delta (Vietnam)	w i	1.0–3035.0								[16]
Polluted European rivers	w i	4.5–45								[16]
Elqui (Chile)	AAS	1705 ± 175*	6082 ± 321	26 ± 1	3 ± 0	445.7	28 ± 2	70 ± 3	147 ± 23	This study

**As; ***Cd, Pb, Cr, Cu; *vMo; vHg; wi: without information.

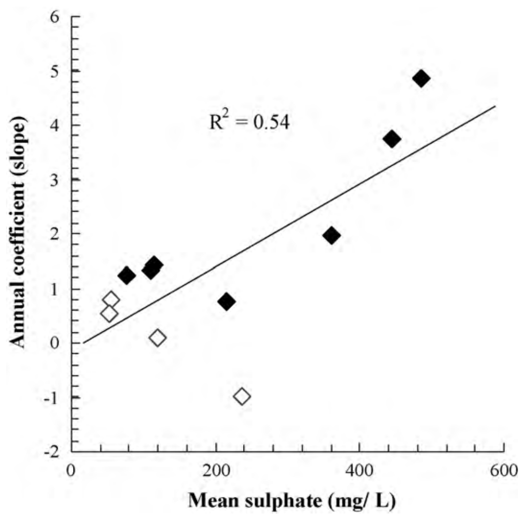

Fig. 3. Scatterplot showing a relationship between annual effect MCMC coefficients on sulfate concentrations and mean sulfate concentrations for 11 different rivers of northern Chile. Filled diamonds represent significant MCMC coefficients (see Table 5).

resulting from interaction between mining pollution, erosion, and natural processes (i.e., weathering or flooding).

Of all the rivers analyzed, the Elqui showed the highest historical mean As, Cu and Pb concentrations. The importance of As and Cu in the Elqui was evidenced through cluster analysis. The Elqui basin concentrates more than 25% of all the large mines in the region, with a large number of gold mines and several copper mines (Table 1). Therefore, it is expected that the Elqui acts as a sink for polluted runoffs from mining activities, including As derived from gold ores and Cu from mining tailings. However, both geological–hydrothermal processes and leaching processes of As–Cu-rich sulphide ores over the last 10,000 years have been suggested as alternative factors explaining the high concentrations of As and Cu in the Elqui [1]. Although the latter two processes may be important to explain the large historical As and Cu means in the Elqui, our results have shown that the concentrations of these two elements are increasing over time (Table 5). Therefore, if it is assumed that geological–hydrothermal processes and leaching tend to be invariant in time, then mining pollution should be the main process contributing to the increasing annual trend in As (and probably in Cu and SO_4^{2-}). These results can be considered robust since Hierarchical Bayesian models, as used in this study, are powerful tools for assessing spatial dynamics processes in aquatic ecosystems [33].

Although it was not included by cluster analysis as a different group, the Rapel had high concentrations of Cu, which can be accounted for by the large number of Cu mines (Table 1). Cu concentration in the Rapel followed a decreasing annual trend (Table 5) that can be explained by improved pollution control and the construction of a mining waste reservoir during the late 80 s. However, although there were not enough data to test for a temporal trend, Mo concentration in the Rapel has probably increased over time (Pizarro, unpublished data).

The Aconcagua was the river with the highest Hg concentration and it also had a high Cr concentration which was determined by cluster analysis. This result is in agreement with the fact that the Aconcagua concentrates almost 25% of all the large mines (especially of copper) in the region. However, it was not possible to determine if the concentration of these two chemical species was increasing over time in the Aconcagua, and further studies should be made.

The results showed that SO_4^{2-} concentration in nine rivers (75%) exceeded 100 mg L^{-1}, and seven different rivers had positive annual slopes. In Chilean rivers such as the Elqui, SO_4^{2-} is a chemical by-product of mining or is derived from the dissolving of sulphate solid phases in xeric areas such as our study site [21,34]. Therefore, wastes from mining activities may be the main cause accounting for the increase in SO_4^{2-} concentration in the rivers. Although the Copiapó and Huasco had the highest SO_4^{2-} concentrations, cluster analysis did not classify them within a distinct group. However, the increase rate of SO_4^{2-} concentration was positively associated with mean sulphate concentration (Fig. 3). Thus, the highly polluted Copiapó and Elqui had slopes >3, indicating that in these rivers SO_4^{2-} is increasing at a high and critical rate.

The concentrations of As, Cu, Hg, sulfate, Cd, Mo and Pb in the Elqui had mean values considerably higher than those reported in other rivers around the world (Table 6). The concentration of As dissolved in the Elqui is ca. 28 times higher than in the Nakkavagu stream in India, 588 times larger than in the Thames in England, and relatively similar to that in the Red river delta in Vietnam (Table 6). Moreover, the Elqui has mean Cu, Hg, Cd, Mo, Pb, and SO_4^{2-} concentrations higher than other rivers in Europe, Asia, and North America, as shown in Table 6. Since As, Cu and SO_4^{2-} concentrations are increasing in the Elqui and the other rivers, the difference between the levels of these chemical species and those in rivers of other continents may become much higher in coming decades.

5. Conclusions

Rivers in central-northern Chile are exposed to pollution from different sources such as mining industry, natural orogenic process, volcanic activity, and geology. However, such pollution sources are heterogeneously distributed within and among basins, as shown by differences in production size and type of mine (Table 1). Our findings suggest that urgent policies are required for controlling and reducing the levels of heavy metals and sulphate in northern Chile. However, pollution management policies should be implemented according to particular pollution sources in each river. Therefore, a necessary condition for monitoring and managing pollution in Chilean basins requires identifying the main sources of heavy metals [35].

The magnitude of water pollution of Chilean rivers is comparable to that of other polluted rivers around the world (Table 6). Particular attention should be given to the Elqui river, which supports the highest pollution levels among the studied rivers, but also concentrates an important agricultural industry (e.g., wine, fruit) and includes areas of international tourist interest. However, the impact of pollution in Chilean rivers may be potentially greater than in other countries due to the aridity of Chile's mining region, which would reduce available water for human consumption and agricultural use. This water limitation may become even more critical if global climate changes reduce local precipitation and affect the hydrological cycles. Decreased rainfall may be crucial in Copiapó, leading to severe restrictions on drinking water, the development of agriculture, and other economic activities in the area.

For these reasons, future research and monitoring programmes should focus on: (1) identifying toxic chemical species and their corresponding pollution points along the rivers; (2) improving sampling frequency and establishing efficient monitoring networks; (3) assessing whether heavy metal input affects the food web structure and dynamics as well as riparian biodiversity; (4) determining if a potential reduction in local precipitation associated with global change will result in increased heavy metal levels.

Acknowledgements

This study was financed by FONDECYT 11080085 and DICYT 09091PK. We thank the Dirección General de Aguas (DGA) for allowing us to use a public data base.

References

[1] S. Carpenter, N. Caraco, D. Correll, R. Howarth, A. Sharpley, V. Smith, Nonpoint pollution of surface waters, Ecol. Appl. 8 (1998) 559–568.
[2] X. Wang, Y. Lu, J. Han, G. He, T. Wang, Identification of anthropogenic influences on water quality of rivers in Taihu watershed, J. Environ. Sci. 19 (2007) 475–481.
[3] B. Muller, M. Berg, Z.P. Yao, X.F. Zhang, D. Wang, A. Pfluger, How polluted is the Yangtze River? Water quality downstream from the three Gorges Dam, Sci. Total Environ. 402 (2008) 232–247.
[4] S. Li, S. Gu, X. Tan, Q. Zhang, Water quality in the upper Han River basin, China: the impacts of land use/land cover in riparian buffer zone, J. Hazard. Mater. 165 (2009) 317–324.
[5] J. Pizarro, P.M. Vergara, P.A. Sanhueza, J.A. Rodríguez, S.A. Castro, Nutrients dynamics in the main river basins of the centre-southern region of Chile, J. Hazard. Mater. 175 (2010) 608–613.
[6] A.H. Dokmeci, A. Ongen, S. Dagdeviren, Environmental toxicity of cadmium and health effect, J. Environ. Prot. Ecol. 10 (2009) 84–93.
[7] J.Y. Kim, B.T. Lee, K.H. Shin, K.-Y. Lee, K.-W. Kim, K.-G. An, Y.-S. Park, J.-Y. Kim, Y.-H. Kwon, Ecological health assessment and remediation of the stream impacted by acid mine drainage of the gwangyang mine area, Environ. Monit. Assess. 129 (2007) 79–85.
[8] C.H. Qu, C.Z. Chen, J.R. Yang, L.Z. Wang, Y.L. Lu, Geochemistry of dissolved and particulate elements in the major rivers of China (The Huanghe, Changjiang, and Zhunjiang Rivers), Estuaries 16 (1993) 475–487.
[9] R. Prego, A. Cobelo-García, Twentieth century overview of heavy metals in the Galician Rias (NW Iberian Peninsula), Environ. Pollut. 121 (2003) 425–1425.
[10] W. Solomons, U. Förstner, Metals in the Hydrocycle, Springer Verlag, New York, 1984.
[11] F. Elbaz-Poulichet, J.-L. Seidel, C. Casiot, M.-H. Tusseau-Vuillemin, Short-term variability of dissolved trace element concentrations in the Marne and Seine Rivers near Paris, Sci. Total Environ. 367 (2006) 278–287.
[12] J.J. Vicente-Martorell, M.D. Galindo-Riaño, M. García-Vargas, M.D. Granado-Castro, Bioavailability of heavy metals monitoring water, sediments and fish species from a polluted estuary, J. Hazard. Mater. 162 (2009) 823–836.
[13] A.K. Krishna, M. Satyanarayanan, P.K. Govil, Assesment of heavy metal pollution in water using multivariate statistical techniques in an industrial area: a case study from Patancheru, Medak District, Andhra Pradesh, India, J. Hazard. Mater. 167 (2009) 366–373.
[14] C. Archer, D. Vance, The isotopic signature of the global riverine molybdenum flux and anoxia in the ancient oceans, Nat. Geosci. 1 (2008) 597–600.
[15] C. Neal, H.P. Jarvie, B.A. Whitton, J. Gemmell, The water quality of the River Wear, north-east England, Sci. Total Environ. 251/252 (2000) 153–172.
[16] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, Appl. Geochem. 17 (2002) 517–568.
[17] P. Higueras, R. Oyarzun, J. Oyarzún, H. Maturana, J. Lillo, D. Morata, Environmental assesment of copper–gold–mercury mining in the Andacollo and Punitaqui districts, northern Chile, Appl. Geochem. 19 (2004) 1855–1864.
[18] R. Oyarzún, J. Lillo, P. Higueras, J. Oyarzún, H. Maturana, Strong arsenic enrichment in sediments from Elqui watershed, Northern Chile: industrial (gold mining at El Indio-Tambo district) vs. geological processes, J. Geochem. Explor. 84 (2004) 53–64.
[19] R. Oyarzun, S. Guevara, J. Oyarzún, J. Lillo, H. Maturana, P. Higueras, 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, Environ. Geochem. Health 28 (2006) 431–443.
[20] J. Tapia, C. Bertrán, C. Araya, M.J. Astudillo, L. Vargas-Chacoff, G. Carrasco, A. Valderrama, L. Letelier, Study of the copper, chromium and lead content in *Mugil Cephalus* and *Eleginops Maclovinus* obtained in the mouths of the Maule and Mataquito rivers (Maule Region, Chile), J. Chil. Chem. Soc. 54 (2009) 36–39.
[21] R. Oyarzun, J. Lillo, J. Oyarzún, P. Higueras, H. Maturana, Strong metal anomalies in stream sediments from semiarid watersheds in Northern Chile: when geological and structural analyses contribute to understanding environmental disturbances, Int. Geol. Rev. 48 (2006) 1133–1144.
[22] E. Schalscha, I. Ahumada, Heavy metals in rivers and soils of central Chile, Water Sci. Technol. 37 (1998) 252–255.
[23] M. Coquery, A. Morin, A. Becue, B. Lepot, Priority substances of the European Water Framework Directive: analytical challenges in monitoring water quality, Trends Anal. Chem. 24 (2005) 117–127.
[24] T. Vila, R.H. Sillitoe, Gold-rich porphyry systems in the Maricunga belt, northern Chile, Econ. Geol. 86 (1991) 1238–1260.
[25] R. Oyarzun, J. Oyarzún, J. Lillo, H. Maturana, P. Higueras, Mineral deposits and Cu–Zn–As dispersion–contamination in stream sediments from the semiarid Coquimbo Region, Chile, Environ. Geol. 52 (2007) 283–294.
[26] T. Dittmar, Hydrochemical processes controlling arsenic and heavy metal contamination in the Elqui river system (Chile), Sci. Total Environ. 325 (2004) 193–207.
[27] SMEWW Standard Methods for Examination of Water and Wastewater, American Public Health Association, Washington, 1995, Method 4500-E.
[28] C.W. Liu, K.H. Lin, Y.M. Kuo, Application of factor analysis in the assessment of ground water quality in a blackfoot disease area in Taiwan, Sci. Total Environ. 313 (2003) 77–89.
[29] D.J. Spiegelhalter, A. Thomas, N.G. Best, D. Lunn, WinBUGS, Version 1.4, Imperial College and MRC Biostatistics Unit, London, UK, 2003.
[30] J.S. Clark, Why environmental scientists are becoming Bayesians, Ecol. Lett. 8 (2005) 2–14.
[31] D.A. Lunn, N. Thomas, D.J. Best, Spiegelhalter, WinBUGS-a Bayesian modelling framework: concepts, structure, and extensibility, Stat. Comput. 10 (2000) 325–337.
[32] S. Sturtz, U. Ligges, A. Gelman, R2WinBUGS: a package for running WinBUGS from R, J. Stat. Soft. 12 (2005) 1–16.
[33] G.B. Arhonditsis, C.A. Stow, L.J. Steinberg, M.A. Kenney, R.C. Lathrop, S.J. McBride, K.H. Reckhow, Exploring ecological patterns with structural equation modeling and Bayesian analysis, Ecol. Model. 192 (2006) 385–409.
[34] L. Romero, H. Alonso, P. Campano, L. Fanfani, R. Cidu, C. Dadea, T. Keegan, I. Thornton, M. Farago, Arsenic enrichment in waters and sediments of the Río Loa (Second Region, Chile), Appl. Geochem. 18 (2003) 1399–1416.
[35] J. Li, H. Ming, W. Han, Y. Gu, Analysis and assessment on heavy metal sources in the coastal soils developed from alluvial deposits using multivariate statistical methods, J. Hazard. Mater. 164 (2009) 976–981.