

Regional hydrogeochemical mapping in Central Chile: natural and anthropogenic sources of elements and compounds

Carmina O. Jorquera^{1*}, Christopher J. Oates², Jane A. Plant³, Kurt Kyser⁴,
Christian Ihlenfeld⁵ & Nikolaos Voulvoulis¹

¹ Centre for Environmental Policy, Imperial College London, London, SW7 2AZ, UK

² Applied Geochemistry Solutions, 49 School Lane, Gerrards Cross, Buckinghamshire, SL9 9AZ, UK

³ Earth Science & Engineering, Imperial College London, London, SW7 2AZ, UK

⁴ Queen's University, Miller Hall, Kingston, Ontario, K7L 3N6, Canada

⁵ Anglo American plc., 20 Carlton House Terrace, London, SW1Y 5AN, UK

* Correspondence: c.jorquera07@imperial.ac.uk

Abstract: Geochemistry is a key tool in identifying sources of elements for both mineral exploration and environmental purposes. This study evaluates the first systematic regional hydrogeochemical survey for environmental assessments of the classic Andean copper mineral province and the Andina–Los Bronces mining district of Central Chile. One hundred and forty-five water samples were collected systematically in the Valparaíso and Metropolitana Regions of Central Chile, including the capital, Santiago. The concentrations of more than 70 elements and compounds were determined using inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC) along with the stable isotopes (δD , $\delta^{18}\text{O}$, $\delta^{34}\text{S}$, $\delta^{18}\text{O}_{\text{SO}_4}$, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{NO}_3}$) and used to define the geochemical baselines in the area and distinguish between different sources. The geochemistry demonstrates the potential to distinguish between natural (bedrock, hydrothermal alteration and mineralization) and anthropogenic (agriculture, sewage and urban) sources of elements. The distribution patterns of many chemicals show a strong correlation with the presence of evaporitic components (Ca, SO_4^{2-} , Sr, K, Rb, total dissolved solids (TDS)), hydrothermal alteration and sulphide mineralization (Cu, Zn, Ni, Cd, Co and REEs). High concentrations of nitrate, phosphate and alkalinity occur downstream of agricultural areas and reflect pollution from fertilizers. Overall, the catchment areas affected by mining activities are relatively small and highly localized compared to those affected by agriculture and urban centres.

Keywords: hydrogeochemical survey, pollution, elements, compounds, stable isotopes, Chile

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Supplementary material: A list of anomalously high element concentrations and specific isotopic compositions associated by source is available at: <http://www.geolsoc.org.uk/SUP18799>

Growing global concern about the impact of pollution on the environment and human health has led to increasingly stringent regulation of levels of potentially toxic elements such as As, Cd, Pb and Hg. Such regulations have been historically based on human health risk assessments and the impacts resulting from exposure to these elements since they were first defined in the 1970s (Vighi *et al.* 2006). This concept evolved in the 1990s with the European Water Framework Directive stressing the protection of the water quality as part of the ecosystem (Vighi *et al.* 2006). Geochemical background values are required when establishing quality criteria for water, sediments and soils (Gałuszka & Migaszewski 2011). The term ‘geochemical background’ derives from exploration geochemistry and is defined as the normal abundance range of an element in barren earth material for a given area (Hawkes & Webb 1962). The term ‘geochemical baseline’ was introduced in 1993 in the context of the International Geological Correlation Programme (IGCP) 259 (Darnley *et al.* 1995) and IGCP 360 to develop a global background database for environmental legislation. Although this term is used sometimes as equivalent to ‘background’, what it measures is ‘ambient background’ or elemental concentration levels at a particular date to be able to quantify future changes (Reimann & Garrett 2005).

Historically, the extent to which the occurrence and levels of these elements are of anthropogenic or natural origin is generally not taken into account in legislation and regulation. This has been changing since modern systematic geochemical databases have been produced such as those by the geological surveys of the UK

and the US (Plant *et al.* 2001); and the demand for those data being increasingly driven by environmental legislation (Johnson *et al.* 2005). Distinguishing the natural occurrence of elements from anthropogenic contributions is a challenge where isotopes and multi-element statistical procedures can sometimes aid (Reimann & Garrett 2005). Therefore, much effort is now being directed at finding appropriate measures, such as those to estimate pre-anthropogenic element levels, and in so doing, to help discriminate between patterns of natural or anthropogenic origin (Reimann & Garrett 2005).

In this study, both multi-element and isotopic analyses were used to prepare a regional geochemical baseline, in line with international standards using systematic sampling of stream water, to distinguish between natural background and anthropogenic pollution and to identify the sources of anomalously high levels of elements.

The area studied is in the mountainous terrain of the Andean Cordillera of Central Chile, which contains a range of Cu–Mo mineral deposits and hydrothermally altered rocks, and in the Central Valley. Valleys in the Andes and in the Central Valley are important for agriculture and human settlements, including the capital of Chile, Santiago. The information obtained in this study provides a detailed understanding of the geochemistry of the region's drainage systems and allows direct comparison of baseline values with international water guidelines and local regulation values. Moreover, the new regional baseline data provide information and evidence necessary for informing future environmental legislation as well as for exploration.

Study Area and Methods

Study area

The research area comprises *c.* 20 000 km² extending from the Andean Cordillera across the Coastal Cordillera including the Central Valley of Central Chile (32°5'S, 69°47'W; 34°19'S, 71°26'W); it covers the La Ligua, Aconcagua and Maipo basins (Fig. 1). The altitude in the region increases markedly from sea level at the west to *c.* 6000 m in the Andean Cordillera in a distance of *c.* 170 km with the highest points being the Tupungato, San Jose and Maipo volcanoes at 6570 m, 5856 m and 5264 m, respectively, and Aconcagua at 6962 m (Fig. 1). The climate is of the temperate Mediterranean type and is characterized by a long dry season in the summer (December–April). Mining activities, mainly copper extraction, take place in the Andean Cordillera (*c.* 3500 m) and Coastal Cordillera (*c.* 800 m). Principal cities, including Santiago city (*c.* 520 m) which has an estimated population of *c.* 7 million (INE 2012) and extends over *c.* 640 km² (Fig. 2), communities and agriculture activities are located in the Central Valley. Livestock rearing takes place in both the Central Valley and the valleys of the Andean Cordillera and Coastal Cordillera.

Geology

The rocks in the area range from Triassic to Tertiary (Fig. 3). Mesozoic stratigraphic units outcrop in N–S bands, along both the Coastal Cordillera and the Andean Cordillera (Figs 2 and 3). The units in the Coastal Cordillera are mainly discordant Cretaceous sedimentary and volcanic rocks of continental origin, and of marine origin in intercalations towards the west (Gana & Wall 1997; Moscoso *et al.* 1982; Piracés & Maksaev 1977; Wall *et al.* 1999). In the Andean Cordillera, the units are mainly concordant Jurassic and Cretaceous marine and continental sediments, associated with extensive evaporites composed mainly of gypsum (Alvarez *et al.* 2000; Charrier *et al.* 2007; Moscoso *et al.* 1982; Rivano *et al.* 1993; Thiele 1980). There are fluvio-alluvial glacial deposits of Quaternary age in the Central Valley (Thiele 1980). The youngest stratified sediments, which are Cenozoic, occur in inactive Pliocene and Holocene volcanic structures and in active volcanoes (Thiele 1980). The oldest Cenozoic stratified units are volcanic and volcano-sedimentary sequences of Lower–Middle Miocene and Oligocene–Miocene, respectively (Charrier 2002; Muñoz *et al.* 2006; Thiele 1980).

Batholiths and stocks ranging in composition from diorites to granodiorites and granites were emplaced in the Coastal Cordillera in Jurassic–Cretaceous. In the Andean Cordillera, plutons and porphyries comprising diorites, granodiorites, granites and monzonites range from Upper Cretaceous to Miocene (SERNAGEOMIN 2003), including Miocene units bearing mineralization of the 'giant porphyry copper' type (Warnaars 1985) which are part of the Late Miocene–early Pliocene porphyry Cu–Mo longitudinal belt of central Chile (Camus 2003; Maksaev *et al.* 2007). The Mesozoic intrusive bodies intrude Mesozoic formations in the Coastal Cordillera, whereas the Cenozoic intrusive bodies intrude Cenozoic and Mesozoic formations in the Andean Cordillera.

Sampling

A suite of 145 stream water samples were collected systematically to international standards (Darnley 1997; Salminen *et al.* 1998) during low flow conditions between February and April 2008. A sampling density averaging 1 sample per 50 km² was used. Samples were collected in HDPE NalgeneTM bottles using a manually-operated peristaltic pump and filtered using AquaprepTM sampling capsules (0.45 µm filter). At each site, separate sub-samples were collected for the determination of cations, anions, stable isotopes (δ D, δ^{18} O, δ^{34} S and δ^{15} N), total dissolved solids (TDS) and total organic carbon (TOC). Samples used to determine major cations and trace elements were acidified with 1 ml of 70% ultra-pure

nitric acid in 60-ml bottles. All samples were refrigerated after collection until dispatched for analysis. Electrical conductivity (EC), pH, dissolved oxygen (DO), temperature and alkalinity were measured in the field.

To control the quality of data, one field duplicate was collected for every 10 samples. One international standard was submitted for every 20 samples and two field blanks were prepared for every 20 samples collected. One of these was added directly to an unwashed bottle and the other was added after filtering.

Analytical techniques

The water samples were submitted to Acme Analytical Laboratories Ltd.[®], Vancouver, for chemical analysis. Samples were analysed for major and trace elements using a 10-ml aliquot directly into an Elan 6000 inductively coupled plasma-mass spectrometer (ICP-MS) if TDS were <0.1%, or diluted by a factor of 10, 100 or 1000 prior to ICP-MS if the TDS value was above 0.1%. Nitrate was determined by a Dionex ICS 2000 Ion Chromatograph (IC) equipped with an IonPac AS 17 separator column and NaOH eluent. Fluoride, EC and pH were determined using an electrode and TDS by meter based on the measurement of EC. Total organic carbon was determined using a Shimadzu TOC analyser.

Isotopic determinations were made at the Queen's Facility for Isotope Research (QFIR) at Queen's University, Canada. Hydrogen isotopes (δ D) were determined in 0.3-ml aliquots using a Thermo Finnigan H-device coupled to a Finnigan MAT 252-MS using a dual inlet. Oxygen-18 signatures (δ^{18} O) in water were determined by analysing 1.5-ml aliquots in a GasBench II coupled to a Thermo Finnigan Delta^{plus} XP-MS using continuous flow. Signatures of the ³⁴S/³²S ratio in sulphate (δ^{34} S_{SO4}) in water samples were determined using a method modified from Wasserman *et al.* (1992). Sulphate in 40 ml of each sample was precipitated as barium sulphate (BaSO₄) by adding 10 ml of a saturated solution of barium chloride (BaCl₂). Carbonates were removed from the precipitate by adding hydrochloric acid (HCl) at 20%, then washed three times with 18 MΩ water to remove residual Cl and dried at 60°C. An aliquot of *c.* 0.5 mg of the precipitate was loaded into tin capsules with 0.5 mg of vanadium pentoxide (V₂O₅) and analysed using a Carlo Erba Elemental Analyser NCS 2500 coupled to a Finnigan MAT 252 IRMS using continuous flow technology. To determine the signatures of the ¹⁸O/¹⁶O ratio in precipitated BaSO₄ (δ^{18} O_{SO4}), *c.* 0.1 mg of BaSO₄ were loaded into silver capsules and analysed by a TC/EA continuous flow technology interfaced to a Thermo Finnigan Delta^{plus} XP-MS with H₂/He auxiliary gas to aid combustion.

To determine the ¹⁵N/¹⁴N ratio (δ^{15} N_{NO3}) and the ¹⁸O/¹⁶O ratio (δ^{18} O_{NO3}) of dissolved nitrate in water samples, the anion NO₃⁻ was precipitated as silver nitrate (AgNO₃) from samples following the procedure of Silva *et al.* (2000). Solute nitrate in the sample was concentrated by passing the 250-ml water-sample through 5 ml of pre-cleaned anion exchanging resin columns. Nitrate was eluted from the anion columns with 15 ml of 3 M HCl in 3-ml increments. The nitrate-bearing acid eluant was then neutralized with silver oxide (Ag₂O), filtered and split into two aliquots; one was evaporated at 60°C to obtain solid AgNO₃ which was analysed for δ^{15} N by a Costech EA interfaced to a Thermo Finnigan Delta^{plus} XP stable isotope ratio mass spectrometer. The second aliquot was separated for subsequent preparation and measurements of δ^{18} O in the nitrate (δ^{18} O_{NO3}).

All oxygen-bearing compounds had to be removed from the aliquot split to determine δ^{18} O_{NO3} accurately. Two ml of 1 M BaCl₂ solution was added to the 13-ml split to precipitate and remove sulphate and phosphate from the sample. The solution was then passed through 5 ml of pre-cleaned cation exchange resin columns in which Ba²⁺ and Ag⁺ are replaced by H⁺. The sample was then neutralized with Ag₂O and the excess of Ag₂O removed from solution by filtering at 0.2 µm. The solution was evaporated at 60°C to obtain solid AgNO₃ which was outgassed for one hour at 100°C in

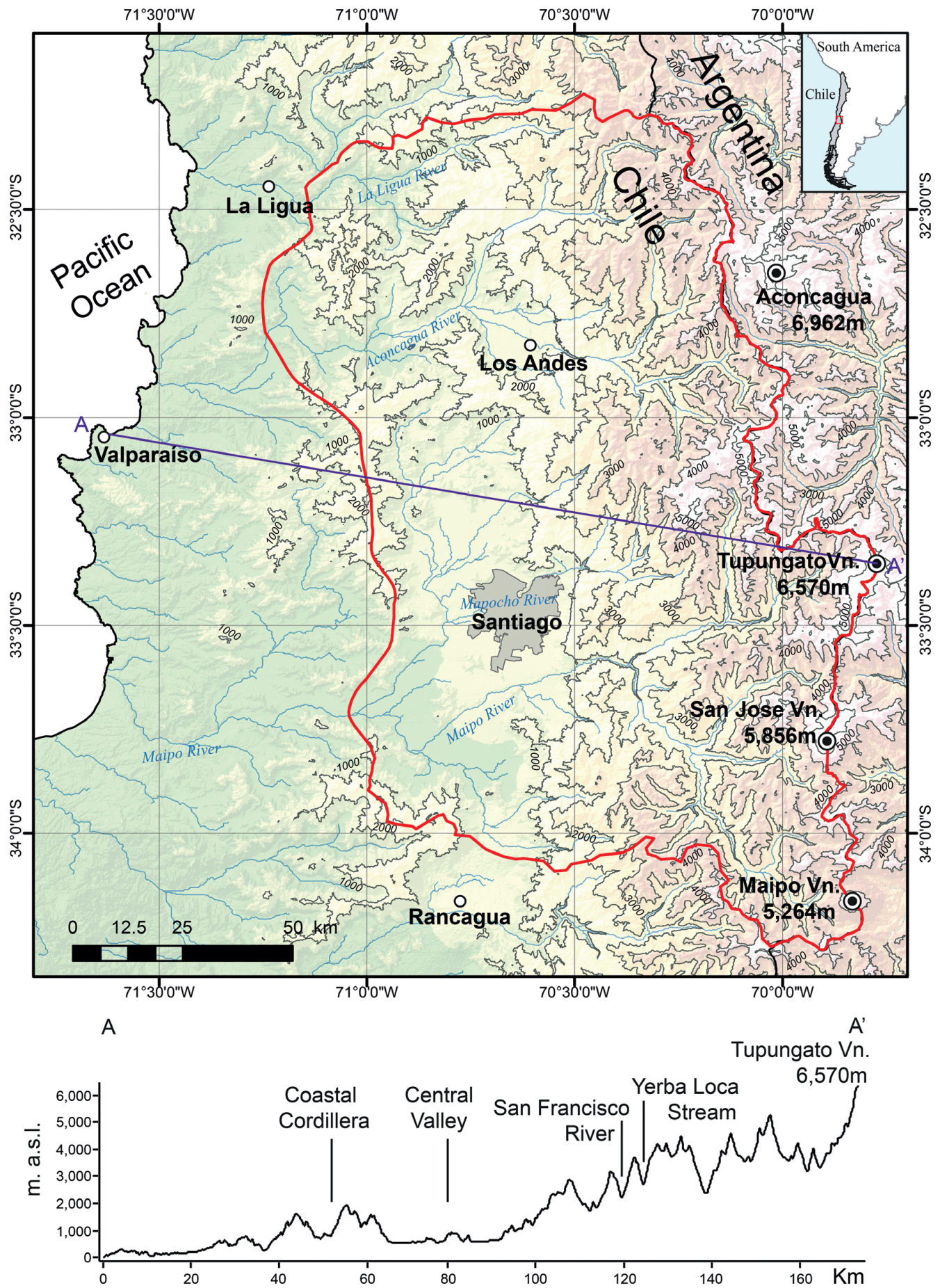


Fig. 1. Contour map showing the highest altitudes on the Chile-Argentina border, Maipo, San Jose and Tupungato volcanoes and the Aconcagua peak. The profile 'AA' highlights the relief of the region. The principal peaks, rivers and valleys are indicated. The study area is outlined in red.

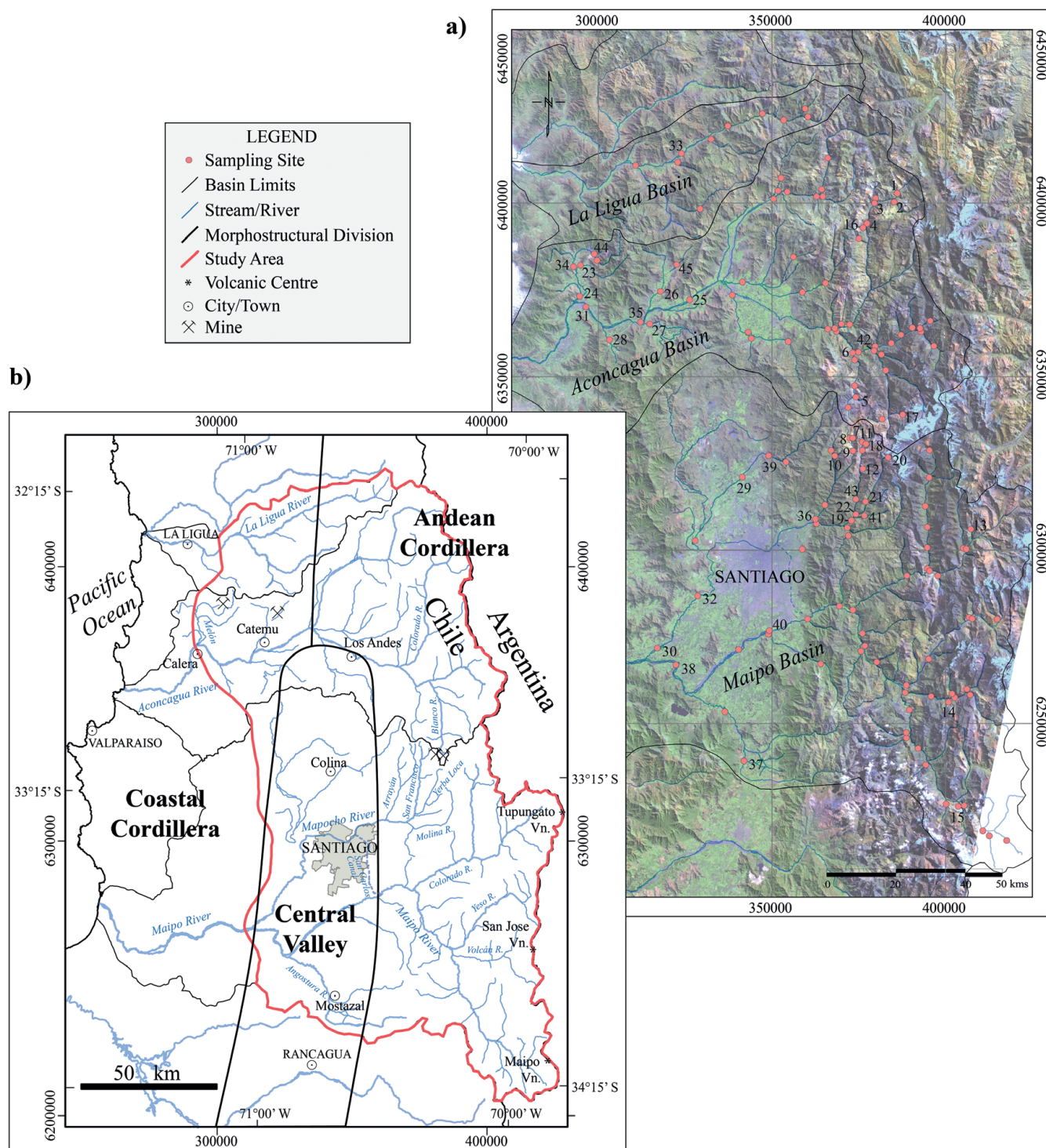


Fig. 2. (a) Sampling sites and outlined basins in the research area south to north: the Maipo, the Aconcagua and the La Ligua basins. Site numbers are shown according to the text and the Supplementary Data. (b) Study area outlined in red and main rivers and streams shown. Catchment basins in thin black lines and morphostructural units outlined in thick black from west to east: Coastal Cordillera, Central Valley and Andean Cordillera.

the oven to remove H_2O . This was then analysed for $\delta^{18}\text{O}_{\text{NO}_3}$ using a TC/EA continuous flow technology interfaced to a Thermo Finnigan Delta^{plus} XP stable isotope ratio mass spectrometer.

The standards used to calibrate the isotope ratios were both in-house and international including NBS127 and NBS123 for $\delta^{34}\text{S}$, NIST8446, NIST8493 and NBS127 for $\delta^{18}\text{O}_{\text{SO}_4}$; NIST8550 and NIST8551 for $\delta^{15}\text{N}$, and NIST8446 and NIST8493 for $\delta^{18}\text{O}_{\text{NO}_3}$.

Alkalinity in the field was measured as HCO_3^- using the digital titrator HACH® model 16900 by both the phenolphthalein and total method (HACH 2006). The CaCO_3 phenolphthalein alkalin-

ity of all of the samples was zero, whereas the total alkalinity measured after adding Bromocresol Green-Methyl Red Indicator represented bicarbonate alkalinity (HCO_3^-).

Quality assurance/quality control (QA/QC)

The reliability of the data was evaluated as a part of a major water dataset comprising 1005 water samples: 100 (10%) field-sample duplicates to determine sampling site reproducibility and precision; 58 (6%) samples of international Certified Reference Materials (CRM) to evaluate the accuracy; 54 (5%) blank samples

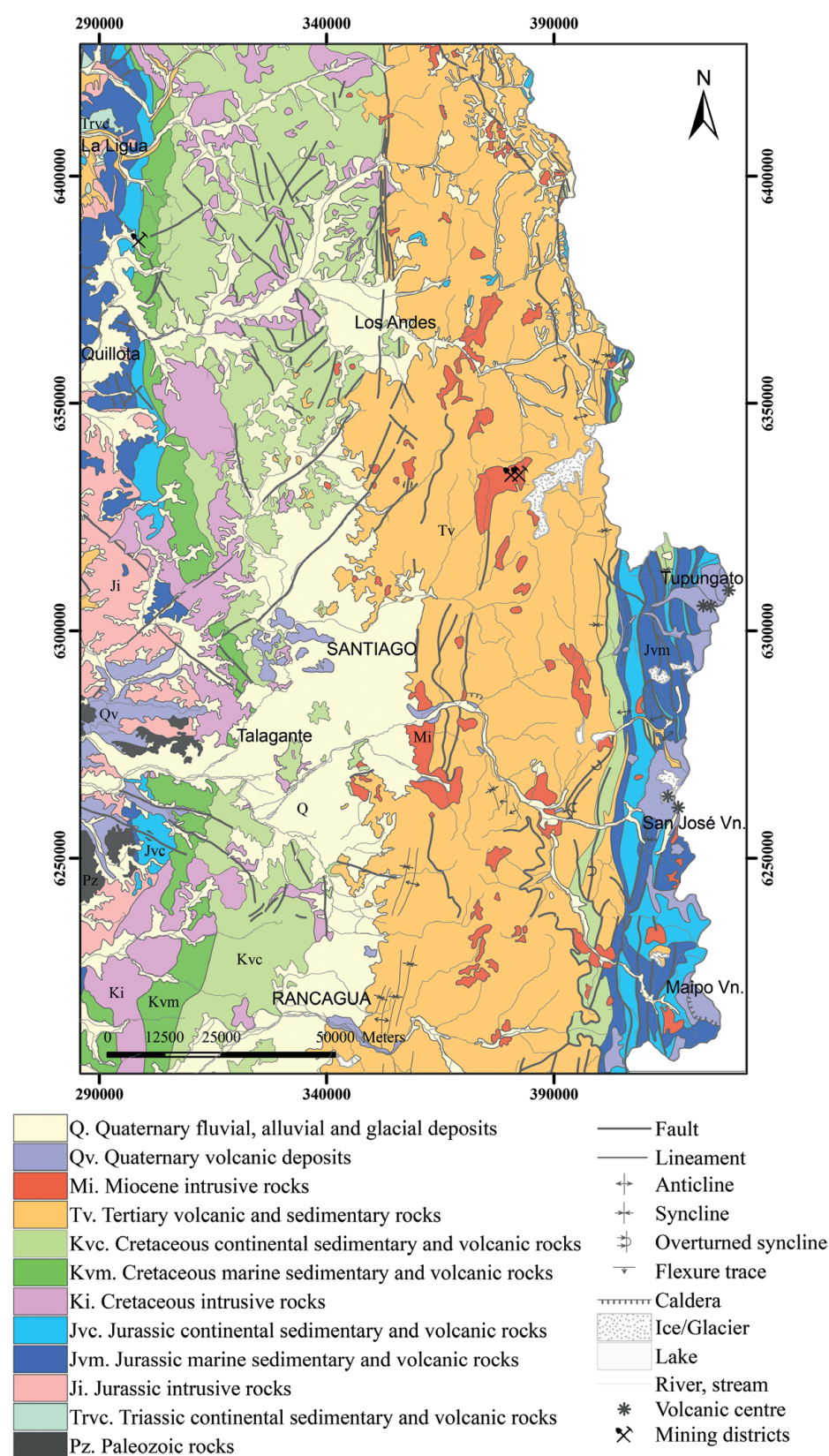


Fig. 3. Geology simplified from SERNAGEOMIN (2003).

prepared in the field to ascertain levels of contamination, during analysis (B1) and 54 (5%) during sample collection (B2).

The CRMs were purchased from the National Water Research Institute of Canada including TM-27.2 and TM-23.3 (lake water) for trace elements determined using ICP-MS and TROIS-94 (river water) for nitrate analysed by IC and physicochemical analyses. Ideally, 95% of all results for the CRM samples should be between ± 2 standard deviations and 99% between ± 3 standard deviations

of the certified mean value. The evaluation showed that TM-27.2 had 94% of samples within the acceptable variation and TM-23.3 had 65%, which reflects the overall better accuracy of TM-27.2 over TM-23.3 for ICP-MS. TROIS-94 had 100% of the samples within the acceptable variability. Only results for Al were significantly outside the acceptable variability; its reproducibility was high with a positive bias of 23% for TM-27.2 and of 36% for TM-23.3. The difference might be partially caused by signal noise

Table 1. Statistical summary and background levels for major ions, selected trace elements and other chemical parameters for the 145 stream water samples. The water guideline values (WGVs) correspond to Chilean drinking water regulated values, to (*) WHO guideline values where no Chilean regulated values were available and to (**) EU-regulated values where no Chilean or WHO were available. The percentage of samples above the WGV is shown in bold

Element/Cpd	Unit	DL	Min	Max	Median	Mean	SD	Background	Mean THLD	WGV	%Samples>WGV
Ag	µg/l	0.05	<0.05	0.16	<0.05	<0.05	0.01	<0.05	<0.05	N/A	N/A
Al	µg/l	1	1	12287	15	325	1482	25	170	200**	6.9
As	µg/l	0.5	<0.5	65.9	3.1	4.7	7.4	3.2	10	10	6.9
Ca	mg/l	0.05	8	377	51	76	71	43	120	N/A	N/A
Cd	µg/l	0.05	<0.05	3.31	<0.05	0.15	0.39	0.07	0.63	10	0
Cl ⁻	mg/l	1	<1	426	8	34	67	12	81	400	0.7
Co	µg/l	0.02	<0.02	88	0.1	3.4	10.7	0.4	6	N/A	N/A
Cu	µg/l	0.1	0.3	11693	1.6	150	1056	6.2	102	2000	2.0
DO	mg/l	0.01	1.78	27.87	14.41	13.37	4.26	12.84	18.02	N/A	N/A
EC	µS/cm	0.1	66	1577	324	440	356	340	940	2500**	0
F ⁻	µg/l	20	22	1010	120	164	136	136	335	1500	0
Fe	µg/l	10	<10	44860	13	528	3822	19	170	300	6.9
HCO ₃ ⁻	mg/l	0	0	220	78	80	52	67	145	N/A	N/A
Hg	µg/l	0.1	<0.1	8.6	0.2	0.4	0.8	0.3	1	1	4.8
K	mg/l	0.05	0.1	25	1	2	3	1.2	3.9	N/A	N/A
Mg	mg/l	0.05	0.8	38	8	10	7	8	20	125	0
Mo	µg/l	0.1	<0.1	38.5	2.1	3	3.8	2.4	8.1	70*	0
Na	mg/l	0.05	0.2	240	12	26	39	12	42	N/A	N/A
Ni	µg/l	0.2	<0.2	59.1	<0.2	2.8	7.9	0.5	5	70*	0
NO ₃ ⁻	mg/l	0.05	<0.05	34	0.31	2	5.5	0.5	3	50	0
P ⁻	µg/l	20	<20	9021	34	134	60	34	67	N/A	N/A
Pb	µg/l	0.1	<0.1	4	<0.1	0.2	0.5	0.1	0.8	50	0
pH	pH	N/A	2	9	7.8	7.6	1.1	7.8	6.5-9	6.5-8.5	13.8
Sb	µg/l	0.05	<0.05	1.01	0.14	0.19	0.19	0.13	0.32	N/A	N/A
SO ₄ ²⁻	mg/l	3	12	1360	114	204	229	99	314	500	8.3
TDS	mg/l	2	34	1524	287	391	320	290	783	1500	0.7
TOC	mg/l	1	<1	10	1	1.2	1.4	1	2	N/A	N/A
Zn	µg/l	0.5	<0.5	345	1.5	21	54	3.9	28	3000	0
δD	‰V-SMOW	N/A	-137	-54	-108	-107	16	N/A	N/A	N/A	N/A
δ ¹⁸ O	‰V-SMOW	N/A	-18.7	-7.5	-14.8	-14.5	2.3	N/A	N/A	N/A	N/A
δ ³⁴ S	‰CDT	30 †	-4.2	14.3	4.9	5.5	4.3	N/A	N/A	N/A	N/A
δ ¹⁸ O _{SO4}	‰V-SMOW	30 †	-8	27.2	6.4	5.6	6.4	N/A	N/A	N/A	N/A
δ ¹⁵ N	‰Air	2 ‡	-1.5	11.9	4.3	4.5	3.5	N/A	N/A	N/A	N/A
δ ¹⁸ O _{NO3}	‰V-SMOW	2 ‡	7.8	40.4	27.2	26.2	9.8	N/A	N/A	N/A	N/A

Cpd, Compound; THLD, threshold; EC: electrical conductivity; TDS, total dissolved solids; V-SMOW, Vienna Standard Mean Ocean Water; CDT, Canyon Diablo Troilite; N/A, not applicable; (†) mg/l SO₄²⁻; (‡) mg/l NO₃; δ³⁴S: n = 109; δ¹⁸O_{SO4}: n = 104; δ¹⁵N and δ¹⁸O_{NO3}: n = 28.

near the detection limit (DL) as values for TM-27.2 were close to ten times the DL; however, the values for TM-23.3 were significantly higher than the DL and showed exactly the same behaviour. It is not clear what caused these differences but Al was interpreted diligently in the data analysis.

The field sample duplicates were considered precise if at least 95% of their percentage relative differences were within a variability of ±20% for concentrations above 10 times the DL of each analyte. Fifty-eight analytes had concentrations below 10 times the DL such as nitrate and the REEs. The evaluation showed that 7 (9%) of the 79 elements and compounds determined had less than 95% within the ±20% of variation, these being Al, B, Ba, Cu, Mn, S and Zn. Of these, Zn was found to be least precise with 63% of the relative differences within the limits while others vary between 89 and 94%. This issue is thought to be caused by signal noise near the DL. The overall average percentage relative difference of the dataset is 8%, which reflects that the overall behaviour is well within the acceptable variation of ±20%, demonstrating a high level of overall precision.

Distilled water and ultra-pure deionized water were used as blank materials. Samples of B1 were prepared by filling Nalgene® sample bottles directly, and samples of B2 were collected as normal water samples by pumping and filtering the blank materials through the sampling equipment. Contamination was considered significant if concentrations in blank samples were higher than 10 times the

DL. The evaluation of B1 and B2 showed that between 82% and 88% of elements and compounds had concentrations below the maximum acceptable level for both distilled and deionized water samples. For distilled water, nine elements had one or more values above 10 times the DL for B1 (B, Ba, Cu, Li, Mn, Pb, Si, Sr and Zn) and 10 elements for B2 (Al, B, Ba, Cu, Li, Mn, Sb, Si, Sr and Zn). For deionized water, 14 elements had one or more values above 10 times the DL for B1 (Al, Ba, Ca, Ce, Cu, Hg, Na, Rb, Si, Sn, Sr, Zn and Zr) and 14 elements for B2 (Al, Ba, Ca, Ce, Cu, Hg, Mn, Na, Rb, Si, Sn, Sr, Zn and Zr). However, no carryover from the sample analysed previously and/or from the previous field sample analysed was detected for any of these elements. Overall, the B1 and the B2 results are closely similar for both distilled and deionized water allowing for the normal analytical variation close to the DL. Therefore, the tubing, bottles and filters have not contributed any contaminating elements to the analytical results.

Overall, the results demonstrate good accuracy and precision, and therefore a high quality geochemical dataset.

Hydrogeochemical baseline maps and identification of sources

The geographic information system (GIS) software Oasis montaj (Geosoft Inc.) was used to prepare regional hydrogeochemical

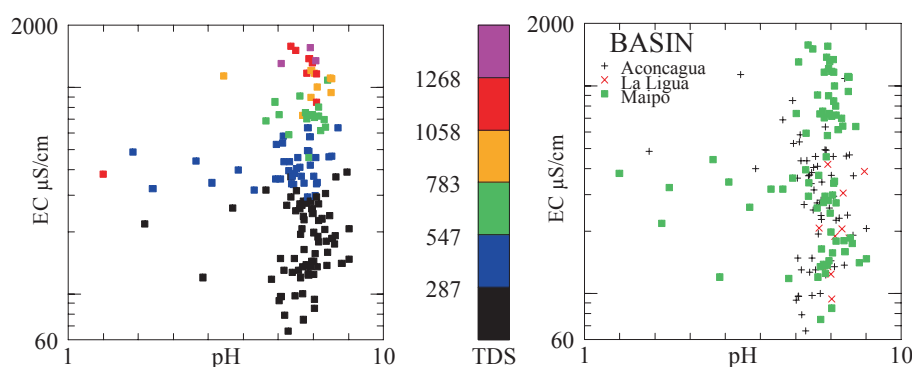


Fig. 4. EC v. pH scatter diagrams for TDS in mg/l (left) and the Aconcagua, La Ligua and Maipo basins (right).

baseline maps in which each sample site represents the chemistry of a catchment area upstream. Breaks in the cumulative probability curve and the frequency distribution of the concentrations of elements (Stanley 1988) were used to select class intervals. Each population or class of a particular parameter was plotted in a different colour. The major population breaks define the thresholds from which the mean background and anomalous concentrations (values above the threshold) were determined (Table 1).

Regional hydrogeochemical baseline maps were prepared for Ca, Mg, K, Al, Fe, Cl, SO_4^{2-} and NO_3^- , and the trace elements As, Cd, Cu, F⁻, Hg, Mo, Ni, P, Pb and Zn, and other key chemical parameters including bicarbonate alkalinity (HCO_3^-), pH and TDS. The geological information (SERNAGEOMIN, AAPlc exploration and mining geological maps), land use, field logging of talus and stream float during sampling and the interpretation of Landsat imagery were used to define the geochemistry of each source and identify and group the anomalously high concentrations of elements and compounds. The sources of dissolved sulphate and nitrate were identified using their stable isotopes. The resulting distributions reflect geology, mineralization and hydrothermal alteration, and anthropogenic sources such as agriculture, human settlements and mining activities. The total area of the watersheds with anomalously high geochemical concentrations was determined for each source identified (Supplementary Data).

Results

Summary statistics for the regional surface water sample data for major ions, selected trace elements, stable isotopes δD , $\delta^{18}\text{O}$ in water, $\delta^{34}\text{S}$, $\delta^{18}\text{O}$ in sulphate and $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ in nitrate and other chemical parameters are presented in Table 1. Electrical conductivity (EC) and pH, measured in the field, ranged from 66 to 1577 $\mu\text{S/cm}$ and 2 to 9 pH, respectively (Table 1). Most of the samples were neutral to alkaline and the main bulk of waters were dilute, with low EC and TDS (Fig. 4). Samples that have neutral to alkaline pH values with high TDS and EC levels were located in the headwaters of the Maipo and Aconcagua rivers draining evaporites, whereas samples which have low pH values with low to high TDS and EC levels were draining mineralization and hydrothermally altered areas in the Maipo and Aconcagua basins.

Most of the elements had median values lower than their mean values (Table 1) which implies that their frequency distribution is skewed to the left. The anomalous ranges for Ca, SO_4^{2-} , Na, K and Cl were identified mainly in the Maipo Basin following a very similar distribution pattern (Ca, SO_4^{2-} , Na, and Cl maps in Fig. 5). Similarly, the distributions of concentrations for NO_3^- , P and HCO_3^- were alike, with the anomalously high values located mainly downstream in the Central Valley and the Coastal Cordillera in agricultural areas (NO_3^- , P and HCO_3^- maps in Fig. 5). The anomalous range of values for As, Al, Cu, Hg, Ni and Zn occurred in a N-S belt in the Andean Cordillera downstream of hydrother-

Table 2. Statistical summary for H, O, S and N isotope values for the La Ligua, Aconcagua and Maipo Basins

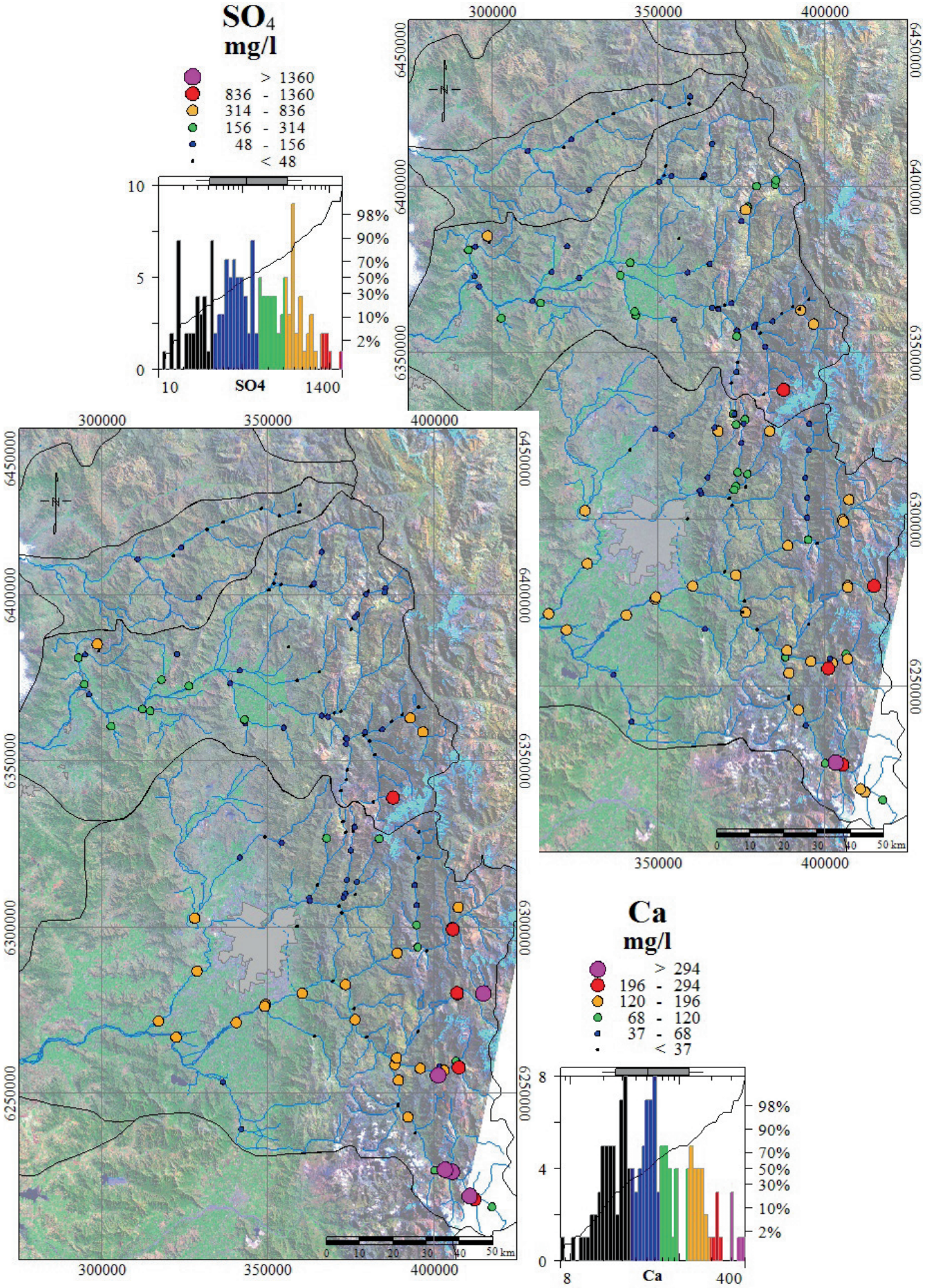
Basin/Stat	δD ‰	$\delta^{18}\text{O}$ ‰	$\delta^{34}\text{S}$ ‰	$\delta^{18}\text{O}_{\text{SO}_4}$ ‰	$\delta^{15}\text{N}$ ‰	$\delta^{18}\text{O}_{\text{NO}_3}$ ‰
La Ligua						
Min	-102	-15	3.4	7.6	4.8	31.3
Max	-64	-8	10.1	18.9	4.8	31.3
Median	-89	-11	5.4	10.2	4.8	31.3
Aconcagua						
Min	-129	-18	-4.2	-8.0	0.0	9.5
Max	-54	-8	11.7	19.8	11.9	34.8
Median	-106	-14	3.5	2.8	4.6	18.1
Maipo						
Min	-137	-19	-3.8	-13.2	-1.5	7.8
Max	-79	-11	14.3	27.2	10.1	40.4
Median	-115	-15	7.1	7.4	3.0	35.6

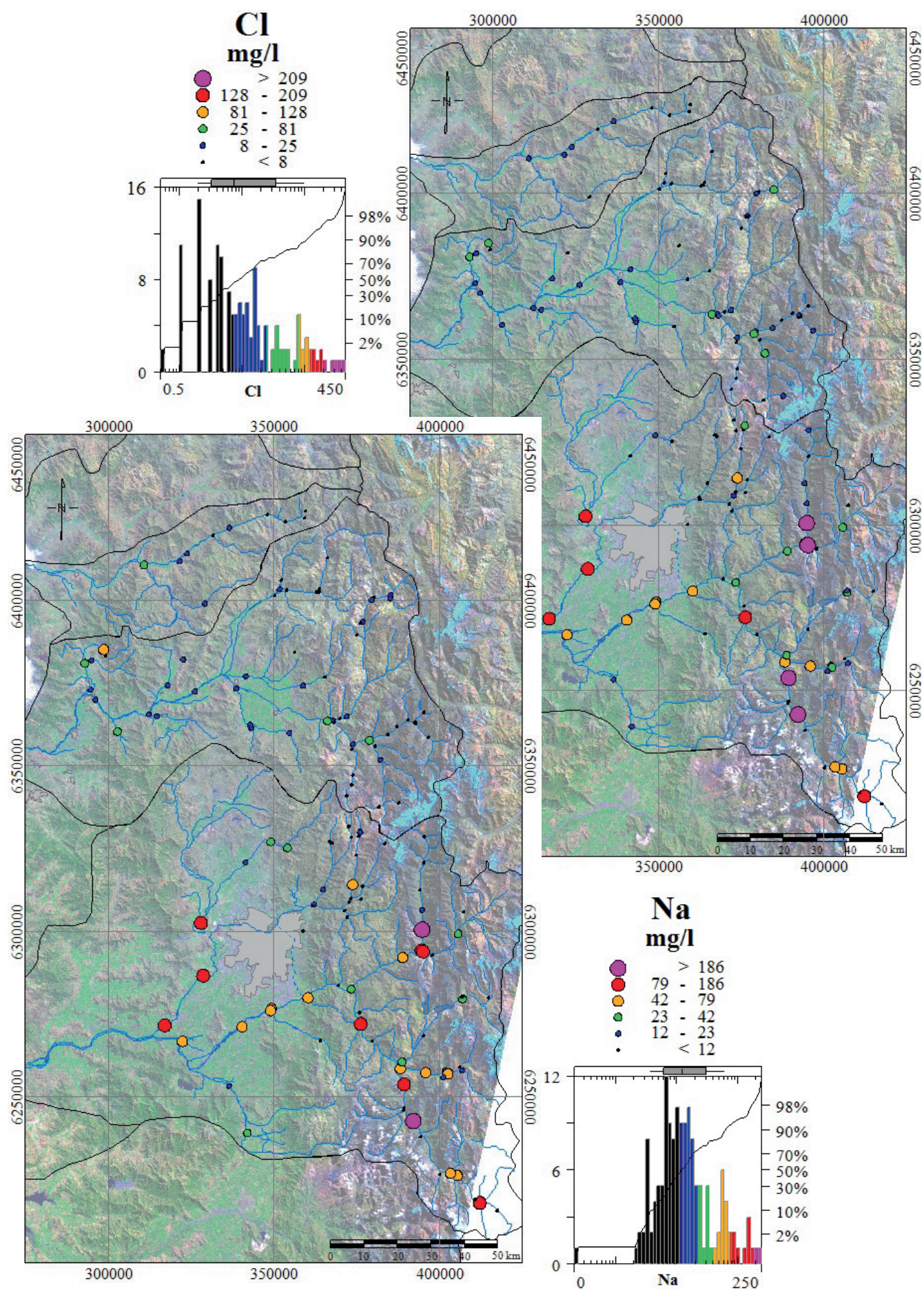
mal alteration areas and mineralization (As, Al and Cu maps in Fig. 5).

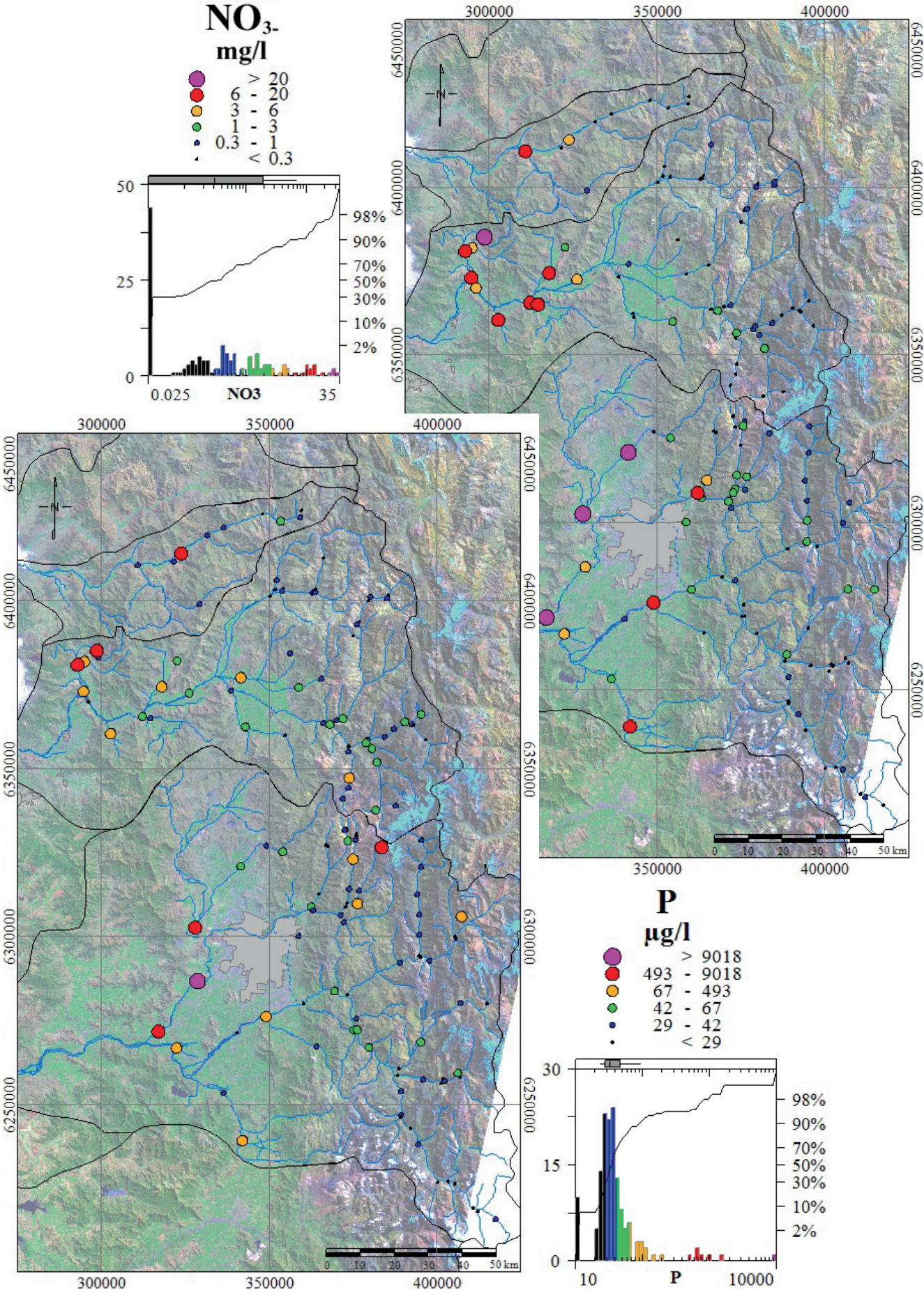
The overall δD values in Central Chile ranged from -137 to -54‰ and $\delta^{18}\text{O}$ from -18.7 to -7.5‰ (Table 1). The La Ligua Basin, with δD and $\delta^{18}\text{O}$ median values of -89 and -11‰, had generally higher values than the Aconcagua Basin, with medians of -106 and -14‰, and the Maipo Basin, with medians of -115 and -15‰, respectively (Table 2). Lower δD and $\delta^{18}\text{O}$ values occurred mainly along the Andean Cordillera whereas the higher values were in the Coastal Cordillera (δD and $\delta^{18}\text{O}$ maps in Fig. 5).

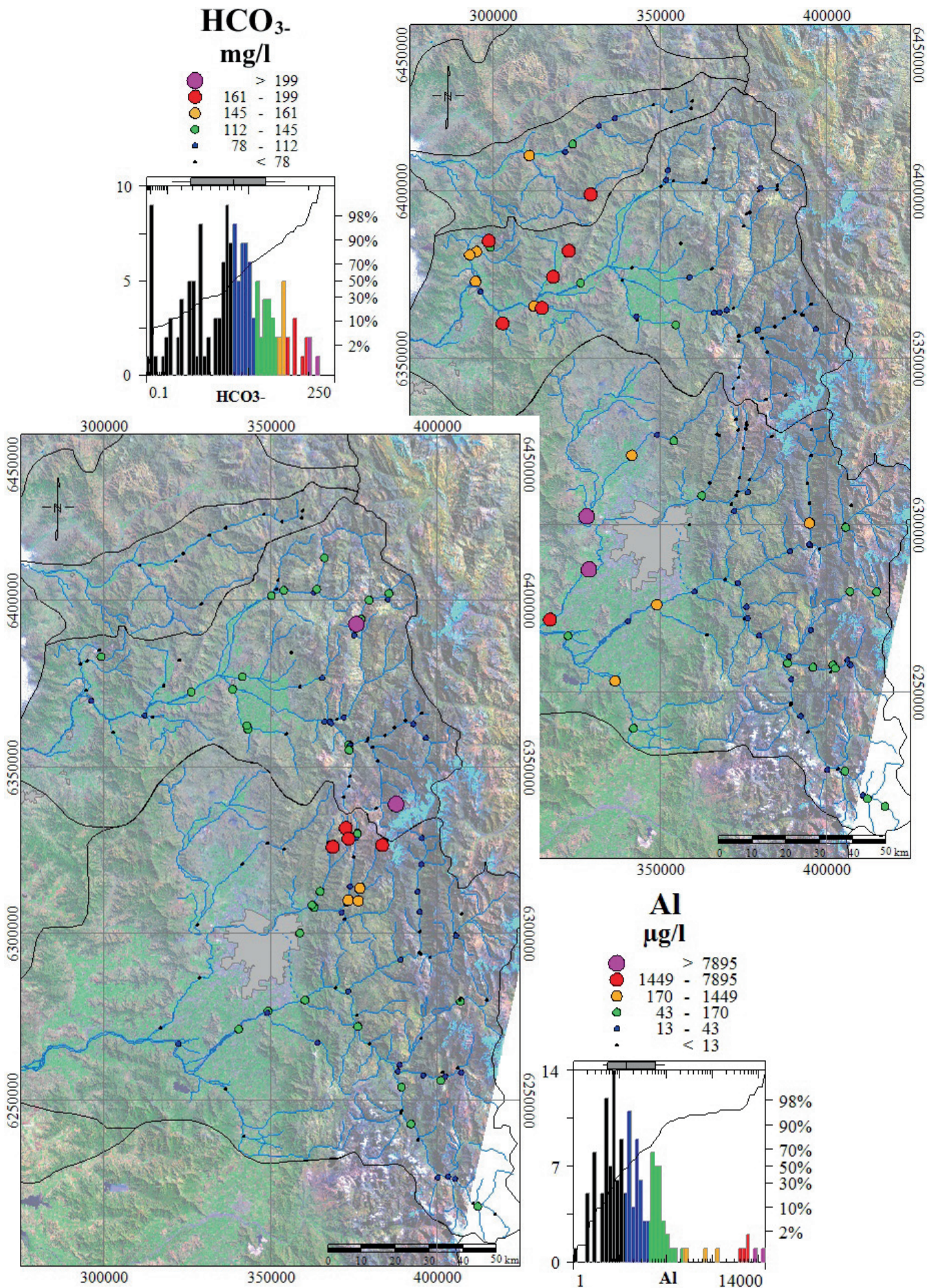
The $\delta^{34}\text{S}$ values of dissolved sulphate in the surface waters of Central Chile ranged from -4.2 to 14.3‰ and the $\delta^{18}\text{O}_{\text{SO}_4}$ values from -8 to 27.2‰ (Table 1). Lower $\delta^{34}\text{S}$ values were located downstream from hydrothermally altered areas whereas higher values were throughout the Maipo Basin ($\delta^{34}\text{S}$ map in Fig. 5). The $\delta^{15}\text{N}$ values of dissolved nitrate in the surface waters of Central Chile ranged from -1.5 to 11.9‰ and the $\delta^{18}\text{O}_{\text{NO}_3}$ values from 7.8 to 40.4‰ (Table 1). Lower $\delta^{15}\text{N}$ values were identified in the Andean Cordillera whereas higher values were identified in the Central Valley and in the Coastal Cordillera ($\delta^{15}\text{N}$ map in Fig. 5). The isotope values obtained for the fertilizers sampled in this study from the Catemu area (Fig. 2) were 2.1‰ $\delta^{15}\text{N}_{\text{NO}_3}$ with 15.6‰ $\delta^{18}\text{O}_{\text{NO}_3}$ for $\text{NH}_4\text{H}_2\text{PO}_4$ (monoammonium phosphate) and -3.4‰ $\delta^{15}\text{N}_{\text{NO}_3}$ for KCl (muriate of potash) with insufficient nitrate to analyse $\delta^{18}\text{O}_{\text{NO}_3}$.

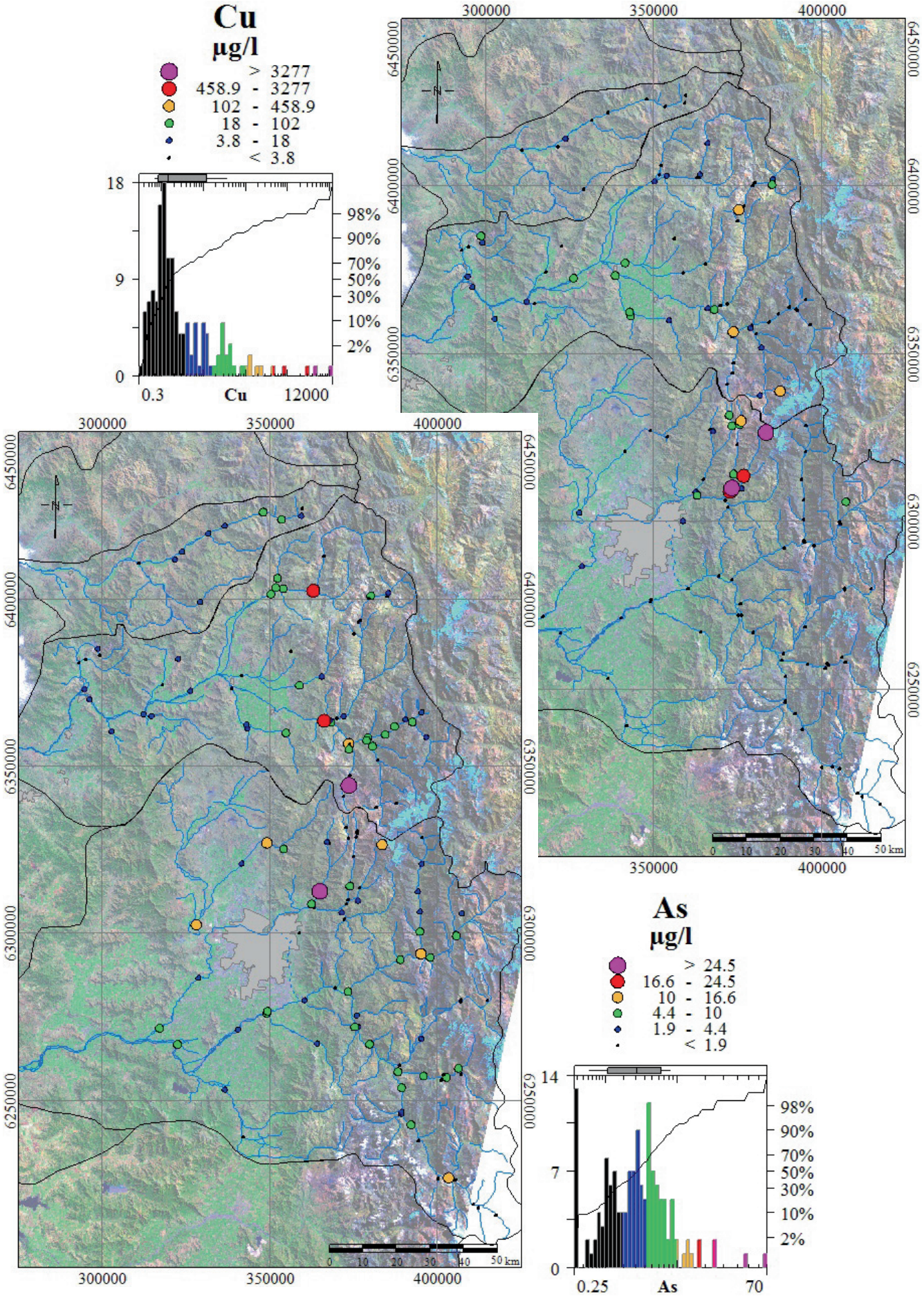
Spearman rank correlation coefficients ρ (r_s) and p-values (p) were calculated for major ions, selected trace elements and other chemical parameters using two-tailed test in MATLAB (Table 3). The critical value of the Spearman's r_s is 0.326 for 100 pairs of data and p-value of 0.001 (Zar 1999). Values were considered to be correlated significantly for ρ values ≥ 0.4 with p-values ≤ 0.001 .

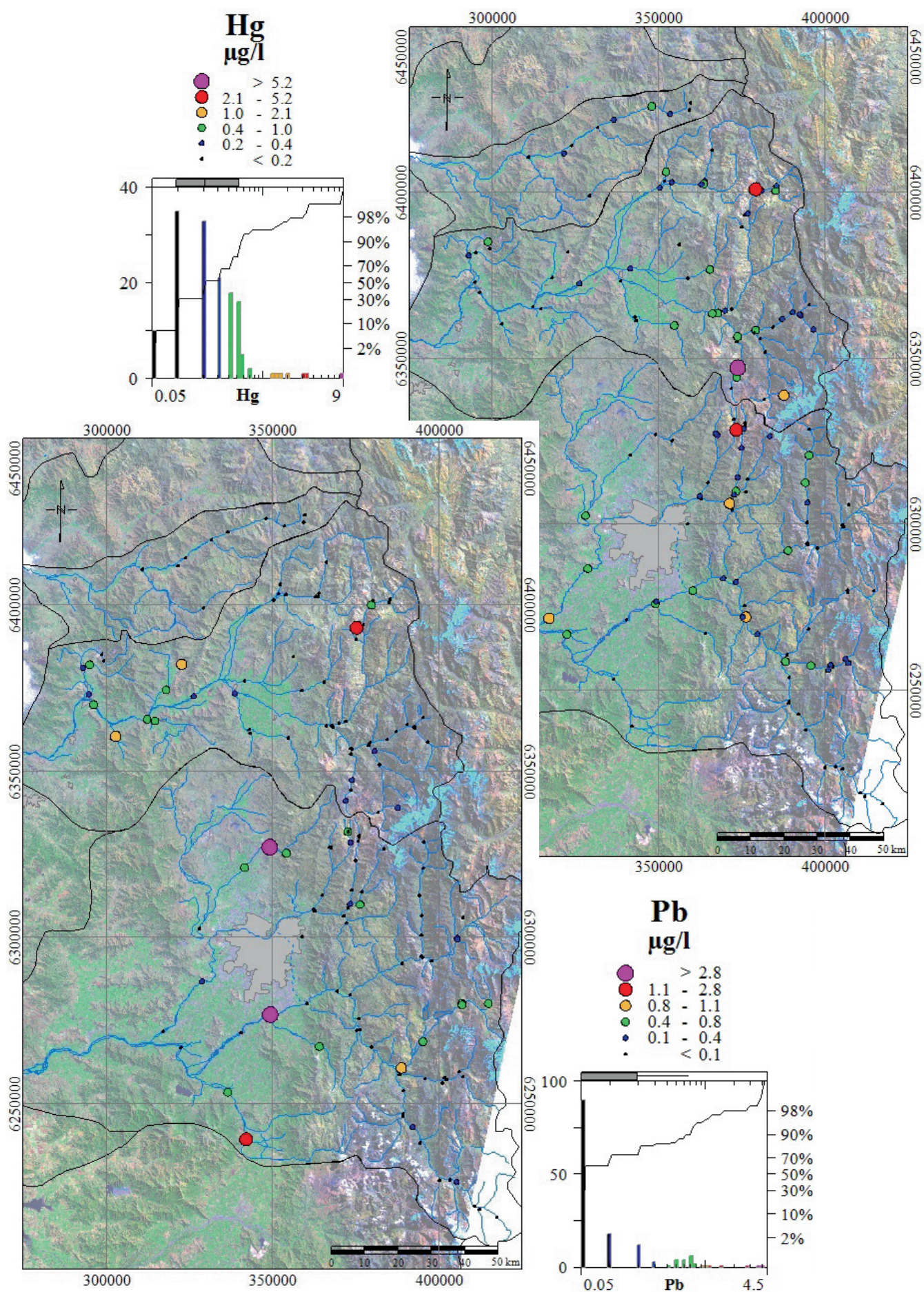


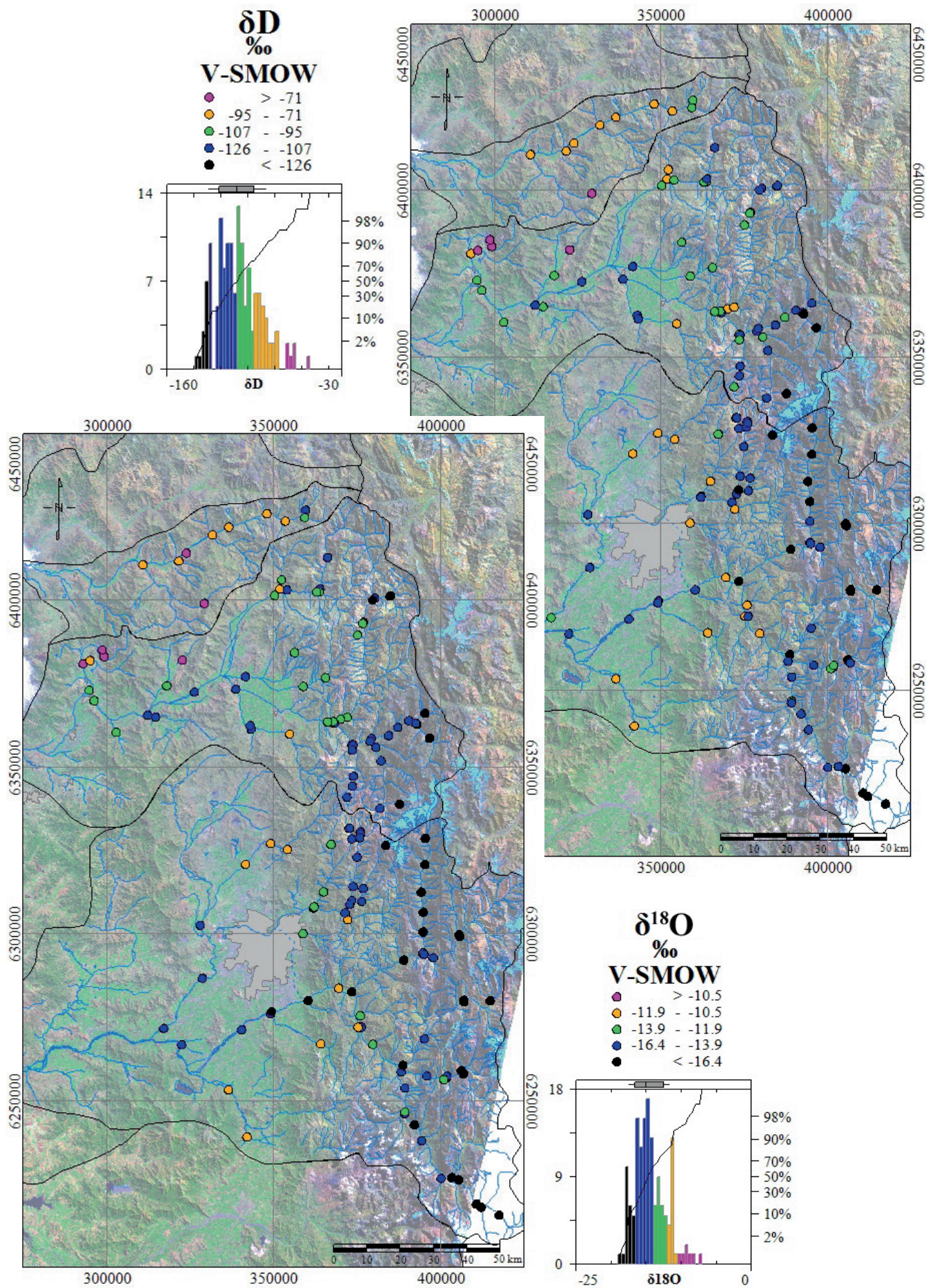












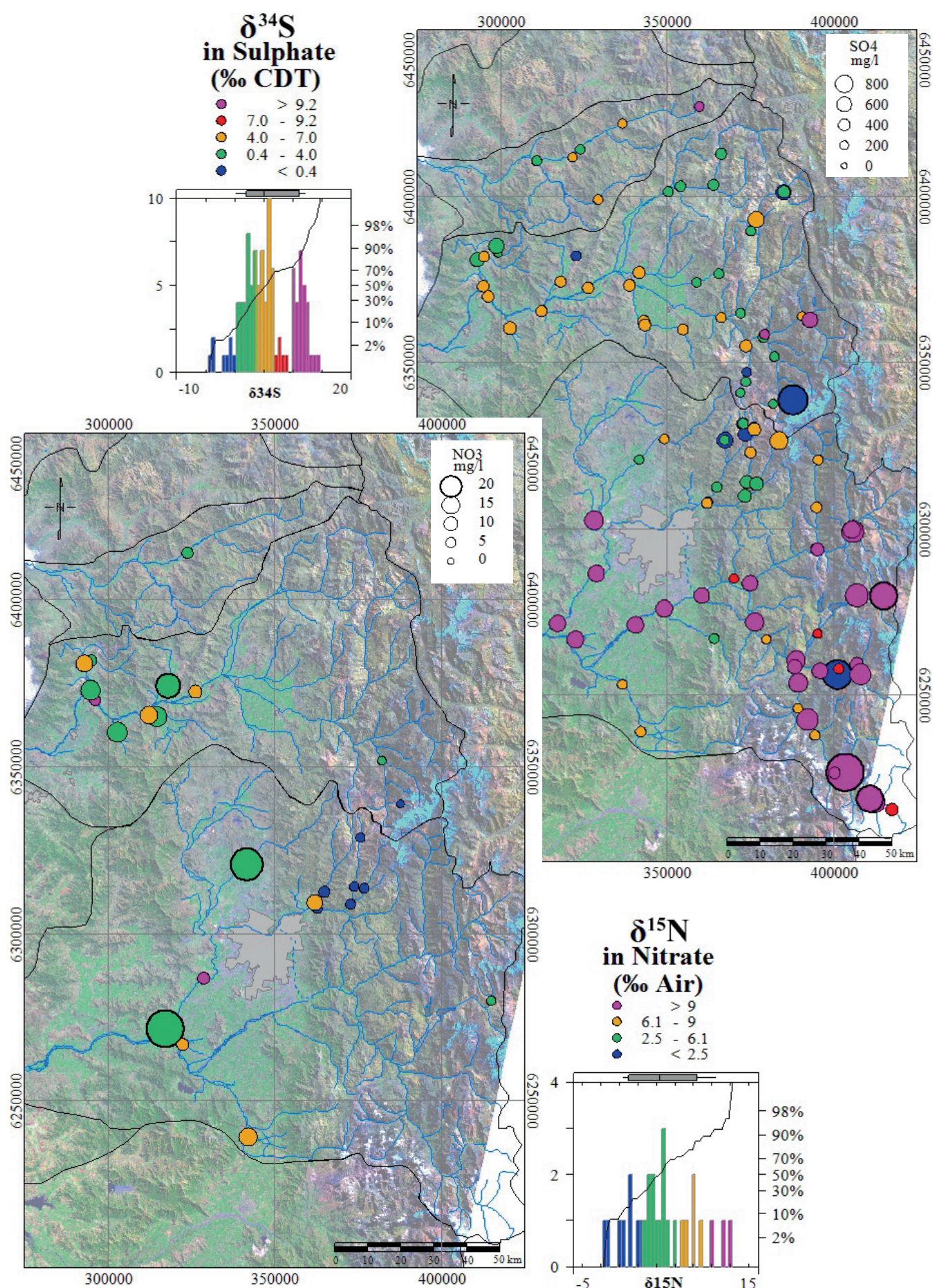


Fig. 5. Stream water geochemical baseline maps coloured in relation to different populations of values for SO_4 , Ca, Cl, Na, NO_3 , P, HCO_3 , Al, Cu, As, Hg, Pb, δD , $\delta^{18}\text{O}$, $\delta^{34}\text{S}$ and $\delta^{15}\text{N}$. Cold colours (black, blue and green) show the background range and the warm colours (orange, red and pink) the anomalous concentrations above threshold. Histograms include the cumulative probability curve and box plot.

Table 3. Spearman rank correlation matrix for chemical parameters. Rho values ≥ 0.4 are in bold

	Al	HCO ₃	As	Ca	Cd	Cl	Cu	EC	F	Fe	Hg	K	Mg	Mn	Mo	Na	Ni	NO ₃	P	Pb	pH	SO ₄	TDS	Zn
Al	1.00																							
HCO ₃	-0.33*	1.00																						
As	-0.13	0.22	1.00																					
Ca	0.26	0.44*	-0.06	1.00																				
Cd	0.49*	-0.50*	-0.35*	0.19	1.00																			
Cl	0.12	0.48*	0.19	0.67*	-0.01	1.00																		
Cu	0.53*	-0.12	-0.30*	0.33*	0.62*	0.17	1.00																	
EC	0.24	0.51*	0.01	0.95*	0.15	0.75*	0.36*	1.00																
F	0.53*	-0.10	-0.22	0.59*	0.39*	0.32*	0.48*	0.57*	1.00															
Fe	0.28*	-0.11	-0.14	0.19	0.21	0.09	0.28*	0.19	0.26	1.00														
Hg	0.11	-0.04	0.18	0.06	0.06	0.14	-0.03	0.09	0.05	0.15	1.00													
K	0.33*	0.33**	-0.02	0.81*	0.19	0.74*	0.37*	0.83*	0.59*	0.21	0.08	1.00												
Mg	0.18	0.57*	-0.11	0.85*	0.15	0.62*	0.34*	0.88*	0.52*	0.19	0.06	0.74*	1.00											
Mn	0.66*	-0.10	-0.26	0.52*	0.59*	0.43*	0.61*	0.52*	0.60*	0.46*	0.09	0.59*	0.50*	1.00										
Mo	-0.07	0.24	0.26	0.39*	-0.11	0.48*	0.02	0.38*	0.23	-0.23	0.00	0.50*	0.21	0.00	1.00									
Na	0.09	0.61*	0.28*	0.63*	-0.04	0.88*	0.18	0.77*	0.31*	0.06	0.09	0.67*	0.68*	0.41*	0.36*	1.00								
Ni	0.48*	-0.26	-0.35*	0.50*	0.67*	0.20	0.54*	0.47*	0.66*	0.43*	0.08	0.46*	0.43*	0.67*	-0.02	0.16	1.00							
NO ₃	0.09	0.43*	-0.06	0.41*	0.11	0.42*	0.46*	0.44*	0.20	0.14	-0.06	0.40*	0.53*	0.36*	0.10	0.45*	0.24	1.00						
P	-0.30*	0.22	0.11	-0.13	-0.14	0.00	0.08	-0.08	-0.24	0.04	0.05	-0.04	-0.02	-0.11	-0.02	0.01	-0.19	0.25	1.00					
Pb	0.05	0.20	-0.19	0.24	0.04	0.06	0.24	0.26	0.16	0.11	-0.18	0.20	0.31*	0.17	-0.02	0.14	0.19	0.33*	0.27*	1.00				
pH	-0.31*	0.41*	0.33*	0.01	-0.49*	0.14	-0.38*	0.04	-0.18	-0.34*	0.04	-0.03	-0.01	-0.41*	0.20	0.19	-0.38*	-0.08	-0.10	-0.20	1.00			
SO ₄	0.44*	0.14	-0.15	0.92*	0.34*	0.55*	0.42*	0.86*	0.75*	0.29*	0.11	0.79*	0.75*	0.64*	0.36*	0.49*	0.64*	0.31*	-0.21	0.26	-0.15	1.00		
TDS	0.27*	0.45*	-0.02	0.97*	0.20	0.71*	0.36*	0.98*	0.61*	0.23	0.07	0.83*	0.88*	0.55*	0.36*	0.71*	0.52*	0.43*	-0.09	0.28*	-0.01	0.90*	1.00	
Zn	0.50*	-0.25	-0.25	0.37*	0.66*	0.14	0.72*	0.35*	0.53*	0.35*	0.07	0.36*	0.29*	0.60*	0.03	0.13	0.65*	0.31*	-0.05	0.27	-0.47*	0.53*	0.39*	1.00

*p ≤ 0.001 **Table 4.** Varimax-rotated loadings for Factors 1 and 2 (eight-factor model) calculated for 145 stream water samples from Central Chile. Loadings above 0.4 and below -0.4 are in bold

	F1	F2
Al	0.145	0.804
As	-0.054	-0.424
B	0.525	-0.326
Ba	0.635	0.064
Br	0.521	-0.223
Ca	0.924	0.066
Cd	0.076	0.804
Cl	0.749	-0.149
Co	0.348	0.838
Cs	0.606	0.322
Cu	0.032	0.829
F	0.639	0.476
Fe	0.133	0.690
HCO ₃	0.216	-0.813
Hg	0.093	0.096
K	0.862	0.097
Li	0.786	0.139
Mg	0.806	0.081
Mn	0.464	0.709
Mo	0.381	-0.472
Na	0.707	-0.214
Nd	0.007	0.916
Ni	0.350	0.805
NO ₃	0.324	0.067
P	0.054	-0.007
Pb	0.160	0.089
pH	0.081	-0.778
Pr	-0.028	0.888
Rb	0.831	0.324
S	0.885	0.311
Sb	0.125	-0.101
Sc	0.035	0.16
Se	0.703	0.04
Si	0.045	0.123
Sr	0.939	0.05
TDS	0.914	0.13
Tl	0.588	0.307
U	0.588	-0.134
V	0.003	-0.549
W	-0.148	-0.136
Zn	0.196	0.813
Zr	0.158	0.297

for the 145 samples. Aluminium, Cd, F, Ni, SO₄²⁻ and Zn were highly positively correlated and probably associated with hydrothermal alteration. Similarly, Cu with Al, Cd, F, Ni, SO₄²⁻ and Zn were highly positively correlated and probably reflecting Cu mineralization. Nitrate, alkalinity and Mg were also highly positively correlated, reflecting agricultural areas.

Factor analysis was determined by excluding those parameters with more than 50% of the sample concentrations below the detection limits and transforming the data to log-centred. The factor loadings were extracted using principal components analysis (PCA) and the results were rotated as varimax-normalized. The first two factors (Table 4) accounted for 52.6% of the total variation. The first factor was highly positively correlated for the alkaline earth metals (Sr, Ca, Mg, Ba), alkali metals (K, Rb, Li, Na, Cs), non-metals (S, Se), halogens (Cl, F) and TDS which dominate the dissolved salts from the evaporites (Fig. 6a). The second factor was highly positively correlated for the rare earth elements (Nd, Pr), transition metals (Co, Cu, Zn, Ni, Cd, Mn, Fe), Al, and highly negatively correlated for the HCO₃⁻ and pH (Table 4), which dominantly reflects dissolved metals from the areas of mineralization and hydrothermal alteration (Fig. 6a).

The scores were calculated for each sample by the factor loadings for both Factors 1 and 2 (Fig. 6b). Samples from the Maipo Basin have groups of samples scoring high for Factor 1, reflecting the presence of evaporites, and Factor 2, reflecting the presence of mineralization and hydrothermal alteration.

Piper ternary diagrams of the major cations in the water samples (Fig. 7) showed the low TDS samples trend to the Ca-type for all three basins, although seven samples from the Maipo Basin, predominantly with high TDS concentration, trend to the (Na+K)-type, reflecting the presence of evaporites. The ternary diagram of the major anions showed the low TDS samples are dominantly of the SO₄-type, trending to the HCO₃-type for all three basins. Some samples with higher TDS concentration are of the SO₄-type, trending to Cl in the Maipo Basin, reflecting also the presence of evaporites. Waters with low TDS levels

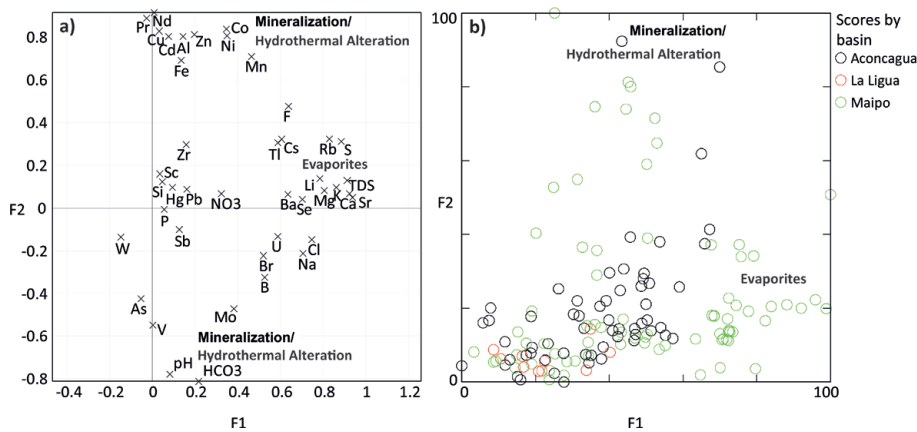


Fig. 6. (a) Factor 1 (F1) v. Factor 2 (F2) with the sources reflected in the results. (b) Sample scores calculated for F1 and F2 for the Aconcagua, La Ligua and Maipo basins. Mineralization, hydrothermal alteration and evaporites reflected in the correlation of the elements in the factors are shown.

that are dominantly of the Ca-HCO₃-type reflect the presence of carbonate rocks in the marine formations and marine intercalations in continental formations in the region. Waters with low TDS values trending to the Mg-Na-HCO₃-type are draining dominantly andesites and granodiorites. Waters with high TDS values, which are dominantly Ca-SO₄ waters trending to the Na-K-Cl-type, reflect interaction with evaporites composed mainly of gypsum.

Discussion

Sources of anomalous geochemistry

The research area for this study extends over *c.* 20 000 km² of Central Chile. Of this, *c.* 5000 km² (25% of the area) was the total calculated area of the watersheds with anomalously high geochemistry. These anomalously high concentrations include one or more of the following parameters: the major cations Ca, Mg, Na, K, Al and Fe; the major anions Cl⁻, NO₃⁻ and SO₄²⁻; the trace elements As, Cd, Cu, F, Hg, Mo, Ni, P, Pb and Zn; and HCO₃⁻, pH, and TDS. To further define the sources, the stable isotopes of hydrogen, oxygen, sulphur and oxygen in dissolved sulphate and nitrogen and oxygen in dissolved nitrate were used. The main sources of these anomalously high levels of chemicals found in stream water were from the natural sources - bedrock geology, hydrothermal alteration, and Cu-sulphide mineralization - and from anthropogenic sources - fertilizer, sewage, human settlements and mining.

Hydrogen (δD) and oxygen ($\delta^{18}O$) isotopes in the stream water samples

The meteoric water line is a linear relationship with a worldwide average defined as $\delta D = 8 \times \delta^{18}O + 10\text{‰}$ relative to SMOW (Craig 1961), but it varies globally (latitude and continental) and locally (altitude and amount of precipitation). The Santiago meteorological water line (SMWL) was obtained from the Global Network of Isotopes in Precipitation (GNIP) database for Santiago station (Fig. 8) of the International Atomic Energy Authority data ($\delta D = 8.279 \times \delta^{18}O - 13.36$). Variation from the meteorological water line indicates evaporation or water-mineral interaction for waters with isotope values below the curve (Fig. 8a).

The relationship between δD and $\delta^{18}O$ in the waters for the three basins is linear and intersects with the SMWL with a slightly smaller slope (Fig. 8). This indicates that the stream waters in all three basins are of meteoric origin and reflects evaporation (Gat 1996) downstream towards the Coastal Cordillera. The La Ligua Basin has the lowest slope (5.922) which reflects the greatest degree of evaporation.

Two end-member sources define the relationship between the δD and $\delta^{18}O$ isotope composition of the water in the three basins:

the first are the highest values ($\delta D > -71\text{‰}$ and $\delta^{18}O > -10.5\text{‰}$) which characterize the waters in the Coastal Cordillera (δD and $\delta^{18}O$ maps in Fig. 5) and have an isotopic composition closer to seawater (0‰). The second end-member source has the lowest values ($\delta D < -126\text{‰}$ and $\delta^{18}O < -16.4\text{‰}$) which characterizes the waters in the headwaters of the Andean Cordillera and reflects depletion of deuterium (D) and ¹⁸O during fractionation of the meteoric water as would be expected for precipitation far from the coast at high altitude.

The high δD (-95 to -71‰) and $\delta^{18}O$ (-11.9 to -10.5‰) values in the Coastal Cordillera and along the west side of the Andean Cordillera reflect the composition of meteoric water away from the Pacific Ocean and at high altitude. The lower δD (-126 to -95‰) and $\delta^{18}O$ (-16.4 to -11.9‰) values along the Andean Cordillera and downstream in the Central Valley reflect meteoric water distal to the seawater source as a result of the rainout effect (Clark & Fritz 1997) that favours the preferential loss of D and ¹⁸O which is also favoured with the continental and altitude effects as explained below.

The influence of the topography from the coast towards the Andes on the isotopic fractionation of H and O isotopes in the waters is seen more clearly in a diagram against east coordinates and altitude (Fig. 9). The continental effect causes coastal precipitation to be enriched in the heavy isotopes but to become more depleted as the vapour mass moves eastward over the continent (Fig. 9a). Altitude also affects isotopic fractionation (Fig. 9b) as reflected in the values for samples along the west side of the Andes (δD and $\delta^{18}O$ maps in Fig. 5). As vapour rises and cools at higher altitudes over the Central Valley, precipitation occurs depleting D and ¹⁸O in the vapour. The combination of these effects can be seen in Figure 9c where the altitude and the east coordinate show a nearly exponential relationship and δD decreases with both.

Sulphur and oxygen isotopes in sulphate

The relationship between $\delta^{34}S$ and $\delta^{18}O_{SO_4}$ in the waters reflects the mixing of different sulphur sources including sulphides, sulphates, fertilizers and detergent and the $\delta^{18}O_{SO_4}$ indicates mixing with atmospheric oxygen in the waters (Fig. 10a). Three end-member sources define this isotopic relationship; the first source, sulphates, has high $\delta^{34}S$ (>9‰) and $\delta^{18}O_{SO_4}$ (*c.* 14‰) values trending towards the signature of the Jurassic evaporites ($\delta^{34}S$ of *c.* 17‰ CDT and $\delta^{18}O_{SO_4}$ of *c.* 13‰ V-SMOW; Claypool *et al.* 1980). This source characterises the waters draining the Upper Jurassic marine evaporites in the marine and continental sediments which outcrop in the headwaters of the Maipo and Aconcagua basins in the Andean Cordillera (Fig. 3) and downstream from this source in the Maipo Basin ($\delta^{34}S$ map in Fig. 5).

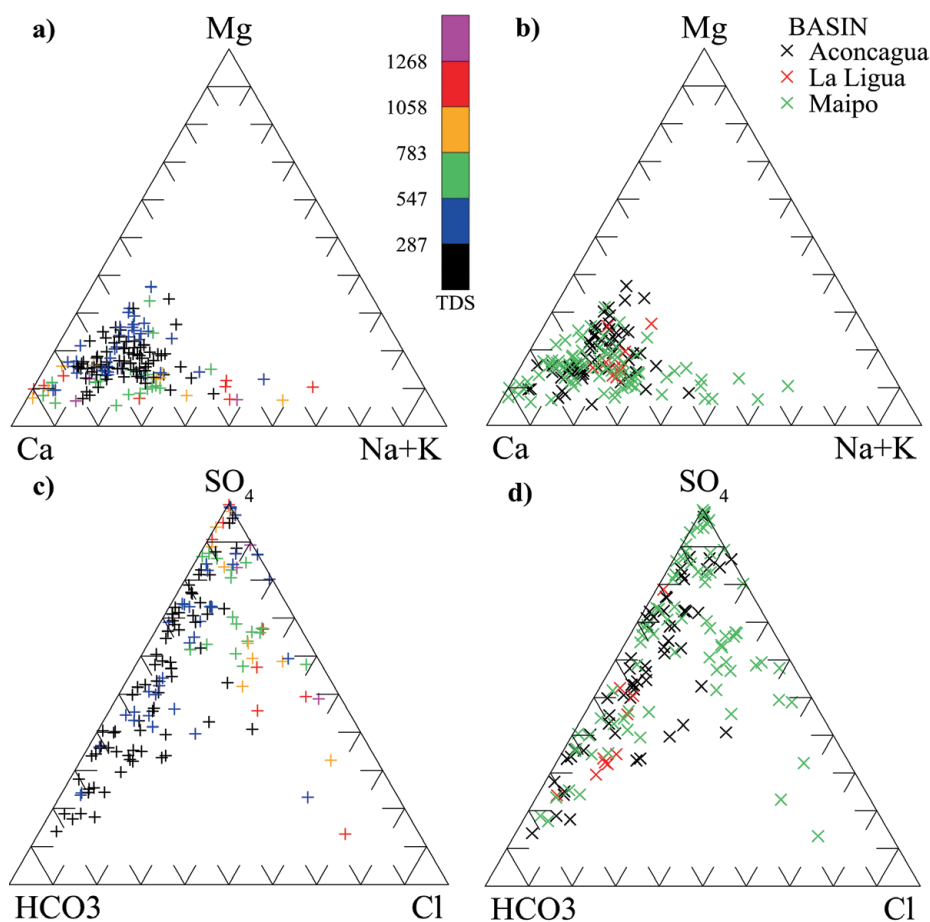


Fig. 7. Ternary diagrams of (a, b) major cations and (c, d) anions coloured by TDS content in mg/l and by basin: Aconcagua (black), La Ligua (red) and Maipo (green)

The second end-member source, sulphides, has much lower $\delta^{34}\text{S}$ (<5‰) and $\delta^{18}\text{O}_{\text{SO}_4}$ (c. 0‰) values, reflecting the leaching and oxidation of sulphides in igneous rocks ($\delta^{34}\text{S}$ c. 0‰ CDT) (Fig. 10a). Oxidation of sulphides by bacteria involves oxygen from surface water and atmospheric $\text{O}_{2(\text{aq})}$ and is accelerated by the exposure of fresh sulphides to weathering resulting in a higher content of $\delta^{18}\text{O}\text{-H}_2\text{O}$ compared to $\text{O}_{2(\text{aq})}$ (Wright & Nordstrom 1999). This source reflects the presence of waters draining areas of hydrothermal alteration, sulphide mineralization (Fig. 3) and mining in the Andean and Coastal cordilleras ($\delta^{34}\text{S}$ map in Fig. 5).

The third end-member source shown by the variation of the oxygen (-8 to +27‰) in the sulphate indicates a mixture of atmospheric oxygen ($\delta^{18}\text{O}\text{-O}_{2(\text{aq})} = 23.5\text{‰}$ V-SMOW) and oxygen in the water molecule ($\delta^{18}\text{O}\text{-H}_2\text{O} = \text{c. } -18 \text{ to } -7\text{‰}$ V-SMOW, in Table 1). Aqueous sulphate reflect the $\delta^{18}\text{O}_{\text{SO}_4}$ values of the evaporite source (Upper Jurassic evaporites c. 10 to c. 15‰ V-SMOW) mixing with the oxidation of sulphides by bacteria, and with sulphate from fertilizers and detergents downstream (Fig. 10a); however, the exact amount of these sources cannot be estimated.

Nitrogen and oxygen isotopes in nitrate

The relationship between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ in the waters is complex and indicates at least two mixing lines between three main end-member sources, including atmospheric nitrate, sewage and fertilizers from agriculture (Fig. 10b).

The first end-member source has low $\delta^{15}\text{N}$ (<-1.5‰) and high $\delta^{18}\text{O}_{\text{NO}_3}$ (>40‰) and is isotopically similar to nitrate deposits in the Atacama Desert ($\delta^{15}\text{N}$ -4.9 to 4.1‰ and $\delta^{18}\text{O}_{\text{NO}_3}$ 36 to 50‰, after Böhlke *et al.* 1997). The accumulation of nitrate in the Atacama Desert has been shown to have been produced by photochemical reactions in the atmosphere using the ^{17}O isotope analysis in nitrate (Michalski *et al.* 2004). This suggests that the

deposition of nitrate in the Andean Cordillera of Central Chile could also be derived predominantly from atmospheric photochemical reactions; however, the very low nitrate concentration (mean of c. 2 mg/l) suggests that these values reflect considerable dilution (Jorquera *et al.* 2012). This source is characteristic of the sample waters collected at high altitudes (2000 to 4000 m) in the Andean Cordillera ($\delta^{15}\text{N}$ map in Fig. 5).

The second end-member source, manure and septic waste, has much higher $\delta^{15}\text{N}$ values (>12‰) with $\delta^{18}\text{O}_{\text{NO}_3}$ (<15‰) (Fig. 10b). The $\delta^{18}\text{O}_{\text{NO}_3}$ values of these samples are systematically higher than values typical of manure and septic waste; however, this is most likely due to mixing with $\delta^{18}\text{O}_{\text{NO}_3}$ derived from the atmosphere (Kendall 1998; Jorquera *et al.* 2012). Even though $\delta^{15}\text{N}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ increase systematically, the content of nitrate does not decrease, and hence there is no evidence of denitrification. A previous study of nitrogen and oxygen isotopes in groundwater of the north Santiago aquifer found values ranging from 3.7 to 12.5‰ for $\delta^{15}\text{N}$ and from 1.8 to 7.17‰ for $\delta^{18}\text{O}_{\text{NO}_3}$ and that the main source of nitrate was from the sewage system (Iriarte *et al.* 2009). This is consistent with the isotope values found in the Mapocho River downstream of Santiago, although the $\delta^{18}\text{O}_{\text{NO}_3}$ values are generally higher in this study. This source reflects the presence of sewage in the area, principally in the Central Valley ($\delta^{15}\text{N}$ map in Fig. 5).

The third end-member source is fertilizers, which have low $\delta^{15}\text{N}$ (<2.5‰) with $\delta^{18}\text{O}_{\text{NO}_3}$ (<15‰) values trending towards those typical of ammonium fertilizers, and high $\delta^{15}\text{N}$ (<10‰) and $\delta^{18}\text{O}_{\text{NO}_3}$ (<25‰) values for nitrate fertilizers (Fig. 10b). The isotope values measured for fertilizers in this study are consistent published values (Kendall 1998), but differ from the Chilean KNO_3 fertilizer isotopic values in another study (Vitòria *et al.* 2004). This source is associated with the agricultural areas in the Central Valley ($\delta^{15}\text{N}$ map in Fig. 5).

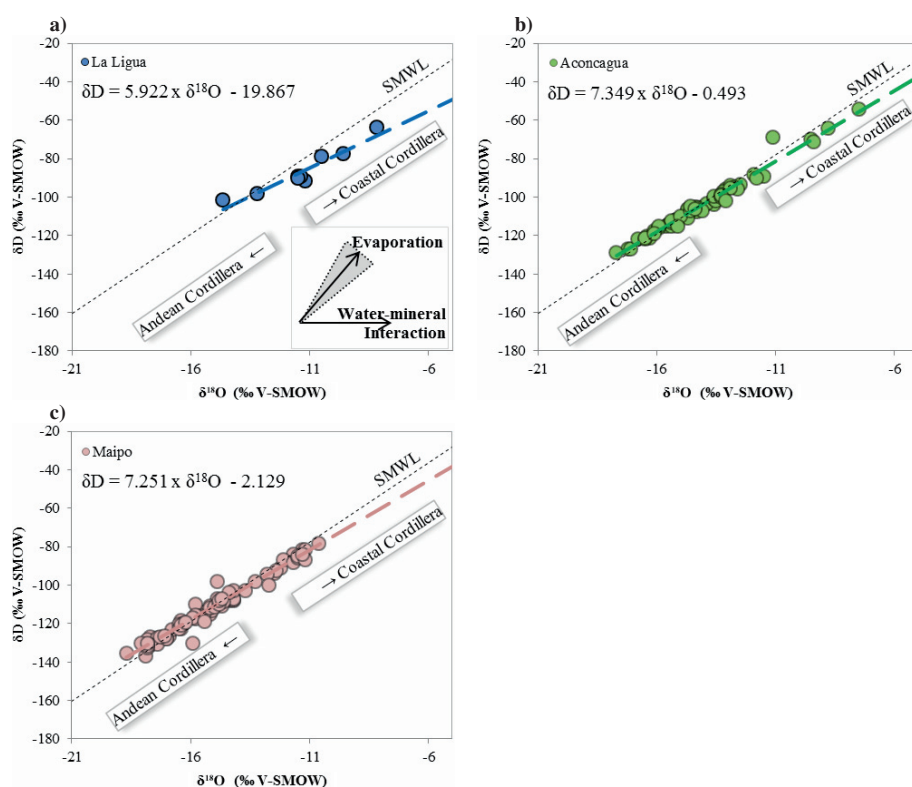


Fig. 8. δD v. $\delta^{18}O$. Black dotted line represents the SMWL of $\delta D = 8.279 \times \delta^{18}O - 13.36$. General trend for samples collected in the Andean and Coastal Cordillera are indicated by arrows. (a) The La Ligua Basin values, regression line ($R^2 = 0.908$; $n = 10$) shown segmented. (b) The Aconcagua Basin values, regression line ($R^2 = 0.976$; $n = 60$) shown segmented. (c) The Maipo Basin values, regression line ($R^2 = 0.974$; $n = 75$) shown segmented.

Table 5. Chilean regulation values in mg/l for drinking (INN 2005) and irrigation water (INN 1978), which are the total maximum concentrations that are allowed for chemical species and compounds. Also shown for comparison are the World Health Organization drinking water guideline values (WHO 2008), and the US (EPA 2009) and the European (EC 1998) regulation values for drinking water. In brackets are the cosmetic and aesthetic guideline values

Chemical Species	Drinking-Water – Health – (cosmetic/aesthetic)				Irrigation
	Chilean	US-EPA	EU	WHO	Chilean
Al	--	(0.05-0.2)	(0.2)	--	5
As	0.01	0.01	0.01	0.01	0.1
Cd	0.01	0.005	0.005	0.003	0.01
Cl ⁻	(400)	(250)	(250)	--	200
Cu	2	1.3	2	2	0.2
EC			(2500)		750-7500
F ⁻	1.5	4.0-(2.0)	1.5	1.5	1.0
Fe	0.3	(0.3)	(0.2)	--	5.0
Pb	0.05	0.015	0.01	0.01	5.0
Mg	125	--	--	--	--
Mn	0.1	(0.05)	(0.05)	(0.4)	0.2
Hg	0.001	0.002	0.001	0.006	0.001
Mo	--	--	--	0.07	0.01
Ni	--	--	0.02	0.07	0.2
NO ₃ ⁻	50	44	50	50	--
pH	(6.5–8.5)	(6.5–8.5)	(6.5–9.5)		5.5–9.0
TDS	(1500)	(500)	--	--	500–5000
Na	--	--	(200)	--	350
SO ₄ ²⁻	(500)	(250)	(250)	--	250
Zn	3	(5)	--	--	2.0

Geology

The major ion geochemistry of the stream waters in Central Chile is dominated by their interaction with evaporites, carbonates in marine sediments, andesites and granodiorites as interpreted from the ternary diagrams (Fig. 7) and the geology

(Fig. 3). The evaporites, which outcrop over a large area in the headwaters of the Maipo and Aconcagua Valleys, comprise mainly Upper Jurassic gypsum inter-bedded and as diapirs with Jurassic stratified volcano-sedimentary rocks, carbonates and marine formations. The carbonate rocks in marine sedimentary rocks also outcrop in the Coastal Cordillera (Fig. 3). Andesites and granodiorites are the dominant rock type in the Andes, whereas marine sedimentary rocks dominate in the Central Valley.

Stream waters dominated by the geochemistry of evaporites extend over a catchment area of *c.* 3600 km² mainly in the Maipo Basin. These waters are Ca- and SO₄²⁻-dominant, trending to the Na-K-Cl-type (Fig. 7a-c) with high TDS of up to *c.* 1500 mg/l and neutral pH values of 7–8.5 and as defined by Factor 1 (Fig. 6). These waters also have anomalous concentrations of Ca, Cl, K, Na, SO₄²⁻ and TDS (Ca, Cl, Na and SO₄²⁻ maps in Fig. 5). The high $\delta^{34}S$ values (9 to 14‰) and the $\delta^{18}O_{SO_4}$ (5 to 15‰) values are consistent with an evaporitic sulphate source for the waters (Fig. 10a). A previous study found values of 11.9‰ for $\delta^{34}S$ and 7.9‰ for $\delta^{18}O_{SO_4}$ in the San Carlos Canal diverted from the Maipo River which is also the main source for drinking water in Santiago, for irrigation and consequently for sewage (Iriarte *et al.* 2009), which is consistent with the dominance of dissolved evaporites in the Maipo Basin found in this study (Fig. 10a and $\delta^{34}S$ map in Fig. 5). The $\delta^{15}N$ value of 4.2‰ with a $\delta^{18}O_{NO_3}$ value of 40‰ for these waters indicates that the dissolved nitrate is from atmospheric sources comparable to that in other waters elsewhere in the Andes (Fig. 10b) (Kendall 1998; Michalski *et al.* 2004).

Early Cenozoic volcanic formations that outcrop over a wide area of the Andean Cordillera are an important part of the background geochemistry of the region and are also characterized by the isotopic data. The waters draining these formations from the headwaters of the Maipo River have $\delta^{34}S$ values between 7 and 9‰ with $\delta^{18}O_{SO_4}$ values of *c.* 4‰ to *c.* 19‰ with a mean SO₄²⁻ concentration of *c.* 90 mg/l ($\delta^{34}S$ map in Fig. 5) and are consistent with a volcanic sulphate source ($\delta^{34}S$ *c.* 3‰ to *c.* 15‰ (Clark & Fritz 1997)).

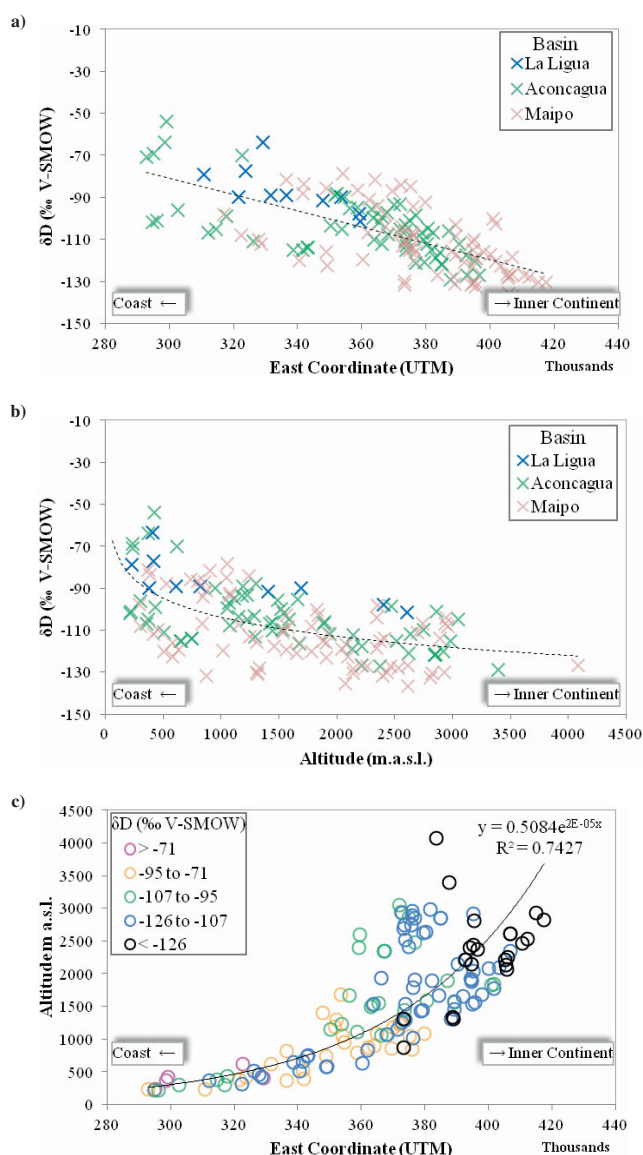


Fig. 9. (a) δD v. east coordinate (E) by basin shows the continental effect. Regression line for all data shown dashed ($\delta D = -0.0004 \times E + 34.944$; $R^2 = 0.46$; $n = 145$). (b) δD v. altitude (A) by basin shows the altitude effect (Clark & Fritz 1997). Logarithmic trendline for all data shown dashed ($\delta D = -13.13 \ln(A) - 13.177$; $R^2 = 0.33$; $n = 145$). (c) Altitude v. E coloured by the distribution of δD . Exponential trendline shown in chart. Central Valley, Coastal and Andean cordilleras indicated.

Hydrothermally altered areas

Fifteen water samples covering c. 380 km² in the Andean Cordillera have a distinctive geochemistry that reflects the influence of extensive areas of hydrothermal alteration. They occur at five locations: in the headwaters of the Colorado, Riecillos, Arrayán and San Francisco rivers, and the area between the Tupungato and Maipo volcanoes (Sites 1 to 15 in Fig. 2 and Supplementary Data). The stream waters reflecting the presence of argillic and propylitic alteration and Zn-Cd mineralization generally have anomalously high values of Al, As, Cd, Fe, Hg, Mo, Ni, SO_4^{2-} and Zn (Al, As, Hg and SO_4^{2-} maps in Fig. 5) with a pH of 3.2 to 8.0, mean 6.5 and variable TDS of c. 150 to c. 1000 mg/l and as defined by Factor 2 (Fig. 6). Similar anomalous chemistry, particularly Ni and Zn, has been found also in groundwaters draining a Cu-porphyry in the north of Chile (Leybourne & Cameron 2000). Waters sampled exactly on the alteration have lower pH (e.g. Arrayán pH 3.2 to

4.7) than those collected farther downstream. This is probably reflecting dilution as the latter mix with fresh waters.

The values of $\delta^{34}S$ in these waters are low (-3.8 to 5.9 ‰, mean 0.7 ‰) indicating that the source of the dissolved sulphate is from oxidizing igneous sulphides (Fig. 10a). These values are within the range (c. 2 ‰– 5 ‰) found in groundwaters draining a Cu-porphyry in the north of Chile (Leybourne & Cameron 2000) and also in those thermal waters in Chile which have a major component of alteration water (Risacher *et al.* 2011). The $\delta^{18}O_{SO_4}$ values (-7.7 – 8.3 ‰, mean 1.3 ‰) are also consistent with waters that have oxidized sulphide sources. The values are generally closer to $\delta^{18}O-H_2O$ compared to $O_{2(aq)}$ which has been also observed in stream waters draining a sulphide ore in the Animas River Basin (Nordstrom *et al.* 2007); this indicates that during the sulphide oxidation most of the oxygen in the sulphate comes from the water.

The percent of dissolved sulphate that came from the oxidation of sulphides was estimated by the isotope-dilution equation and assuming the other end-member source as the evaporites. For the Maipo Basin, the $\delta^{34}S$ end-member values of 14.3 ‰ for evaporites in the headwaters of the Maipo River, -3.8 ‰ for sulphides in the headwaters of the Mapocho River and 12.7 ‰ for these waters mixing downstream of the San Carlos Canal and Santiago were considered. This was also estimated for the Aconcagua Basin, considering $\delta^{34}S$ values of 11.7 ‰ (evaporites dissolved in the Juncal River), -0.2 ‰ (sulphides in the Blanco River) and 4.7 ‰ (mixing of these waters in the Aconcagua River). The percent of dissolved sulphate that is derived from the oxidation of sulphides was estimated as 9 % for the Maipo Basin and 59 % for the Aconcagua Basin. This reflects the dominance of the evaporites over the sulphides in the Maipo Basin whereas in the Aconcagua the contribution of these sources is similar and sulphides are slightly dominating the system.

The values measured for $\delta^{15}N$ of 2 ‰ and for $\delta^{18}O_{NO_3}$ of 34 ‰ in the Arrayán area are in a similar range to those obtained in the evaporites area and are also consistent with an atmospheric source (Fig. 10b).

The oxidation of sulphides produces an acidified environment and releases metals (e.g. Cd, Fe and Hg), metalloids (As), and anions (SO_4^{2-}). Clays (e.g. chlorites, illite, smectite) can break down, releasing Al. Pyrite has been reported as the main hydrothermal source for Fe, SO_4^{2-} , Ni and Co (Plumlee *et al.* 2005). These processes are occurring in the Arrayán and in the headwaters of the streams draining the other hydrothermally altered areas. The concentrations of these elements decrease downstream and the pH increases, reflecting downstream dilution with precipitation, co-precipitation and absorption of the elements with the resultant removal from the water.

The hydrothermally altered areas between the Tupungato and Maipo volcanoes have much higher TDS values (c. 1000) than the other areas (Supplementary Data); these are possibly buffered by the presence of evaporites in this area. The high $\delta^{34}S$ value of 10 ‰ in the Barroso River is an exception and may indicate the dominance of sulphate dissolution from evaporites over the hydrothermal alteration.

At the Agua Mala (Site 5 in Fig. 2), a tributary of the Riecillos River, and in the Barroso River Valley (Site 15 in Fig. 2), local farmers have reported cattle dying after drinking the water and the stream is currently fenced off (field observation). Waters at both sites have relatively high As concentrations (65.9 and $17 \mu g/l$, respectively), higher than the regional background (Table 1). The As content in the surface waters of the Camarones River in the north of Chile is associated with the volcanic activity of the Andean Cordillera (López *et al.* 2012). Volcanic activity is inferred for the Barroso River associated with the Maipo Volcano located nearly 20 km west.

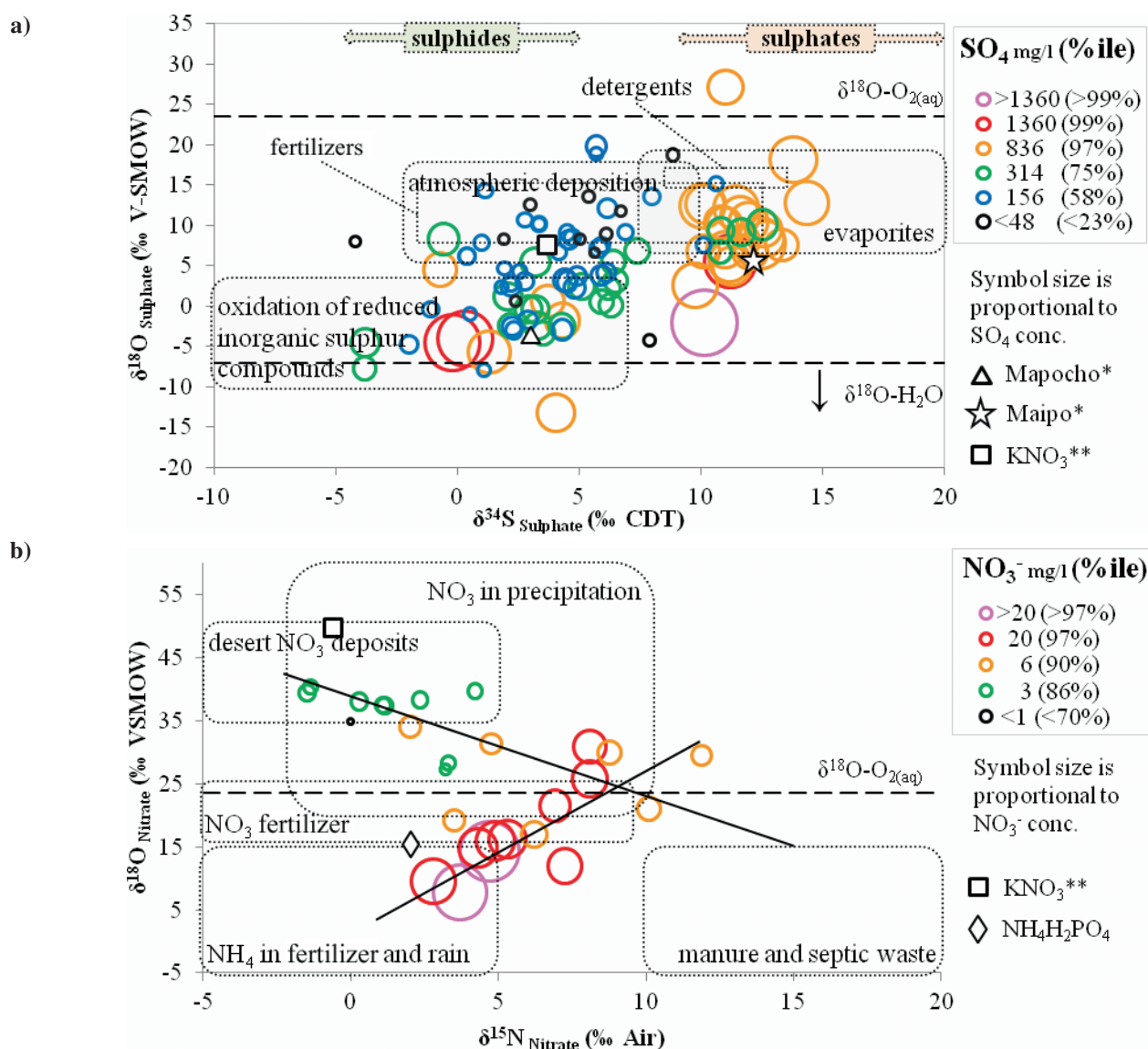


Fig. 10. (a) $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of water samples and typical sulphate sources. The size and colour of the symbol correspond to the concentration by percentile (%ile) of dissolved sulphate in mg/l. Typical $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values are shown by shaded areas (Krouse & Mayer 2000; Vitòria *et al.* 2004) and dashed lines show oxygen isotopic values expected from atmospheric (23.5‰ (Kroopnick & Craig 1972)) and regional meteoric waters (−18 to −7‰, data this project). Previous isotopic data are shown for the Mapocho* and Maipo* rivers (Iriarte *et al.* 2009) and KNO_3 Chilean fertilizer** (Vitòria *et al.* 2004). The $\delta^{34}\text{S}$ range of values for sulphides and sulphates are also indicated. (b) Modified from Jorquera *et al.* (2012). Typical $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of various nitrate reservoirs (after Kendall 1998) shown in boxes. The size and colour of the symbol correspond to the concentration by percentile (%ile) of dissolved nitrate in mg/l. Two possible mixing lines are shown by continuous black lines. Fertilizer isotopic data are shown for the KNO_3^{**} Chilean fertilizer (Vitòria *et al.* 2004) and for $\text{NH}_4\text{H}_2\text{PO}_4$ determined for this study.

Copper mineralization

For the purpose of this study, Cu mineralization is defined by the presence of highly anomalous concentrations of Cu and other Cu mineralization-associated elements in stream waters in areas with no known historic or current mining. Seven water samples from the survey have a distinctive geochemistry reflecting the presence of the copper sulphide mineralization that they are draining at four locations, viz.: Colorado, Barriga and San Francisco rivers and Yerba Loca Stream (Sites 16 to 22 in Fig. 2 and Supplementary Data). These areas extend over a total area of c. 190 km² in the Andean Cordillera. The waters draining these areas have a generally low pH of 2 to 6.6, with a mean 4.8, together with variable TDS of 262 to 1070 mg/l and anomalously high values of Al, Cd, Cu, Fe, Hg, Mg, Ni, Pb, SO_4^{2-} and Zn (Al, As, Cu and SO_4^{2-} maps in Fig. 5) and as defined by Factor 2 (Fig. 6). The chemistry of Cu-mineralization is very similar to that found in this study for hydrothermal alteration with the general difference of lower pH

and anomalous Cu. The results found in groundwaters draining a Cu-porphyry in the north of Chile (Leybourne & Cameron 2000) are also comparable to those presented here, particularly Cu, Ni, Pb, SO_4^{2-} and Zn which are elevated within the Cu-porphyry.

The values of $\delta^{34}\text{S}$ in waters draining Cu mineralization are low (−0.2 to 4.3‰, mean 2.7‰) indicating also that the source of the dissolved sulphate is from oxidizing igneous sulphides (Fig. 10a). As discussed previously for the hydrothermal alteration source, these $\delta^{34}\text{S}$ values are also in the range found in groundwaters draining a Cu-porphyry in the north of Chile (Leybourne & Cameron 2000) and in thermal waters in Chile (Risacher *et al.* 2011). The low $\delta^{18}\text{O}_{\text{SO}_4}$ values (−4.5 to −0.4‰, mean −1.7‰) are also consistent with waters that have oxidized sulphide sources and their proximity to $\delta^{18}\text{O}-\text{H}_2\text{O}$ is explained as most of the oxygen in the sulphate comes from the ambient stream water during sulphide oxidation (Nordstrom *et al.* 2007).

The low values measured for $\delta^{15}\text{N}$ (−1.5 to 0.3‰, mean −0.4‰) and the high $\delta^{18}\text{O}_{\text{NO}_3}$ values (34.8 to 39.4‰, mean 37.4‰) in these

areas have a similar range to those obtained in the evaporites and hydrothermally altered areas and are also consistent with an atmospheric source (Fig. 10b).

In the headwaters of the Yerba Loca stream, the waters sampled closer to the mineralization have the lowest pH of 2 which increases downstream to pH 5 with mixing of fresh waters. Aluminium, As, Ni and P concentrations decrease downstream, reflecting dilution and precipitation, co-precipitation and absorption of these elements as discussed for the hydrothermal areas. Copper and Zn, however, decrease initially downstream but increase slightly upstream of the junction with the San Francisco River, reflecting probably another minor source of Cu mineralization. The anomalously high phosphorous concentration is most likely reflecting the presence of apatite in porphyry copper mineralization (Bouzari *et al.* 2011; Williams & Cesbron 1977), which is soluble in the acid environment and precipitates under more neutral pH downstream.

Agriculture and sewage

The chemistry of 25 stream water samples reflects the presence of agriculture, communities and sewage. These areas, which are in the Central Valley and Coastal Cordillera, cover a total area of c. 710 km². The waters are grouped according to the principal source of nitrate affecting the water chemistry, *viz.*: fertilizers, sewage and a mixture of nitrate sources (Sites 23 to 38 in Fig. 2 and Supplementary Data). These sources were differentiated with nitrogen and oxygen isotopic compositions of the dissolved nitrate (Fig. 10b). Waters draining these areas have anomalously high values of HCO₃⁻, F, K, Mg, NO₃⁻ and P (HCO₃⁻, NO₃⁻, and P maps in Fig. 5) with a pH of 6.6 to 8.5 (mean of 7.8) and a variable TDS of 262 to 1180 mg/l.

Stream water catchments where fertilizers are the principal source of nitrate extend over c. 270 km² in tributaries of the Aconcagua River in the Coastal Cordillera and in tributaries of the Maipo River in the Central Valley (Sites 23–30 in Fig. 2 and Supplementary Data). The low $\delta^{15}\text{N}$ (2.8 to 6.2‰) and $\delta^{18}\text{O}_{\text{NO}_3}$ (7.8 to 19.2‰) values indicate that ammonium and nitrate fertilizers are the principal source of dissolved nitrate (Fig. 10b). The anomalously high concentrations of HCO₃⁻, K, Mg, NO₃⁻ and P are also consistent with the use of fertilizers (Fitzpatrick *et al.* 2007; Ohte *et al.* 2008). The values of $\delta^{34}\text{S}$ (3 to 11‰) and $\delta^{18}\text{O}_{\text{SO}_4}$ (2.5 to 27.2‰) in these waters indicate mixing of a range of sulphate sources (Fig. 10a) including sulphides and sulphates, and anthropogenic sources of fertilizers and household chemicals such as detergents (Krouse & Mayer 2000; Vitòria *et al.* 2004).

The areas where sewage is the main source extend from c. 160 km² in the Aconcagua River near the Calera Township and in the Mapocho River downstream from Santiago (Sites 31–32 in Fig. 2 and Supplementary Data). The high $\delta^{15}\text{N}$ (10.1 to 11.9‰) and $\delta^{18}\text{O}_{\text{NO}_3}$ (21 to 29.5‰) values reflect manure and septic waste with $\delta^{18}\text{O}_{\text{NO}_3}$ systematically higher than the typical values, however (Kendall 1998), which is most likely due to mixing with $\delta^{18}\text{O}_{\text{NO}_3}$ derived from oxygen in the atmosphere (Fig. 10b). These waters are also anomalously high in concentrations of F⁻, HCO₃⁻, K, Mo, NO₃⁻ and P which is related to the presence of agricultural communities and sewage (Muscott & Withers 1996; Neal *et al.* 2010). The $\delta^{34}\text{S}$ (4.8 to 12.7‰) and $\delta^{18}\text{O}_{\text{SO}_4}$ (2.3 to 8.3‰) values also indicate mixing of sulphate, sulphide and anthropogenic sources such as fertilizers (Fig. 10a). Stream water catchments with mixed sources of nitrate extend over c. 280 km² in the La Ligua and Aconcagua rivers in the Coastal Cordillera and in tributaries of the Maipo River in the Central Valley (Sites 33–38 in Fig. 2 and Supplementary Data). The slightly high $\delta^{15}\text{N}$ (4.8 to 8.8‰) and $\delta^{18}\text{O}_{\text{NO}_3}$ (12 to 31.3‰) values in these waters indicate the mixing of nitrate sources including fertilizers, sewage and atmospheric

nitrogen (Fig. 10b). The waters also have anomalously high values of HCO₃⁻, K, Mg, NO₃⁻ and P which are related to the presence of fertilizers, septic waste and detergent in sewage as previously discussed. The $\delta^{34}\text{S}$ (0.4 to 11‰, mean 5.7‰) and $\delta^{18}\text{O}_{\text{SO}_4}$ (3 to 10.2‰) values reflect a mixing of evaporites, sulphide oxidation, fertilizers and household chemicals such as detergents (Fig. 10a).

Phosphate and nitrate are important plant nutrients but their excessive use in agriculture can lead to eutrophication and algal blooms in stream waters and lakes (Edmunds 2009; Muscott & Withers 1996). This, in turn, can lead to the excessive growth of cyanobacterial biomass or blue-green algae generating toxins which are potentially hazardous to human health (WHO 2011). Algal blooms were recorded in most of the Central Valley and eutrophication was recorded locally, particularly in the valleys of the Coastal Cordillera (Field observation). Nitrate concentrations are below water guideline values (WGVs) and P is not regulated in drinking water.

Human settlements

Eight samples have a distinctive geochemistry reflecting the presence of human settlements and other types of built environments that are chemically distinct from the areas affected by sewage and fertilizers. They extend over c. 200 km² in the Central Valley, the Coastal Cordillera and downstream from the ski resorts in the Andean Cordillera. These stream waters have localized anomalously high concentrations of Pb, Hg, or P (Hg, P and Pb maps in Fig. 5) in the vicinity of townships in the Central Valley and the Coastal Cordillera and downstream from the ski resorts in the AC (Sites 28, 30, 37, 39, 40 and 41 in Fig. 2 and Supplementary Data).

The localized highly anomalous concentrations of Pb and Hg, in waters with chemistry dominated by evaporites which are not a source of these elements, are interpreted to be associated with illegal dumping of paint, lead pipes, batteries and the use of pesticides.

Mine area waters

For the purpose of this study, mine area waters are defined as waters derived from natural mineralization sources mixing with fresh water diverted around the enclosed Cu mine areas or, in the case of the La Poza and Restauradora Pb–Zn mineralization, associated with small abandoned mines. They do not reflect the mining operation because all mine and process waters are diverted to tailing dams up to 50 km away in the Central Valley. Additionally, the fresh water streams near the Cu-mines are diverted around mining operations into major streams. Waters downstream from major mines in the district have a near neutral pH and low metal contents. Stream waters near mines which have highly anomalous levels of chemicals reflect the presence of high-grade mineralization and alteration or potential contamination with road dust.

Four samples have a distinctive geochemistry which reflects the presence of mine area waters and extend over c. 60 km². These include the Andina–Los Bronces C–u–Mo districts in the Andean Cordillera and the El Soldado Cu district and the abandoned La Poza and Restauradora Pb–Zn mines in the Coastal Cordillera (Sites 42 to 45 in Fig. 2 and Supplementary Data). These waters have anomalously high concentrations of Cd, Cl, Mo, Na, and Zn with pH values in the range 7.7 to 7.9, with a mean of 7.8 at Andina and Los Bronces; Fe, Mg, Mo and SO₄²⁻ with pH 8.4 at El Soldado; and Pb and Zn values with pH 7.1 in the La Poza and Restauradora abandoned Pb mine areas.

Anomalously high Na and Cl concentrations in these areas in the Andean Cordillera reflect salting of mine roads (field observation). The Cd, Mo and Zn values are thought to reflect a combination of mineralization in the area as well as dust from mine roads adjacent to the rivers. Anomalously high Pb and Zn concentrations reflect the La Poza and Restauradora Pb–Zn mines and are thought to be related to the abandoned smelter in the area. The low $\delta^{34}\text{S}$ values of -1.1‰ to 3.7‰ indicate that the source of dissolved sulphate in these waters is

from sulphide oxidation (Fig. 10a) and are within the ranges found for hydrothermal alteration and mineralization as discussed previously. The low $\delta^{18}\text{O}_{\text{SO}_4}$ values of -3.0‰ to 0.7‰ are also consistent with waters that have oxidized sulphide sources and that the oxygen in the sulphate is mainly from ambient stream water (Nordstrom *et al.* 2007). The near atmospheric $\delta^{15}\text{N}$ value of 1.1‰ and high $\delta^{18}\text{O}_{\text{NO}_3}$ value of 37‰ indicate that the dissolved nitrate is from an atmospheric source in the mine area waters as found elsewhere in the Andean Cordillera where $\delta^{15}\text{N}_{\text{NO}_3}$ ranges from -1.5‰ to 4.2‰ with $\delta^{18}\text{O}_{\text{NO}_3}$ from 34‰ to 39.7‰ and NO_3^- contents from 0.3 to *c.* 4 mg/l. The possibility of a source of nitrate from explosives used in mining was evaluated. However, no measurable contribution of NO_3^- was found from explosives (Jorquera *et al.* 2012). The nitrate isotope values were the same as the isotopic composition of the non-mine-related waters in the Andean Cordillera. Further, the NO_3^- concentrations in the waters sampled in the Andean Cordillera were almost below minimum levels for analytical measurement.

The mine area waters of the San Francisco River *c.* 20 km downstream from the mine operations have values within the background ranges (Table 1) for Al (0.016 mg/l), Cu (41 $\mu\text{g/l}$) and Ni (4.3 $\mu\text{g/l}$), which are lower than the levels at the end of the Yerba Loca Valley of Cu (4185 $\mu\text{g/l}$), Ni (18 $\mu\text{g/l}$) and Al (1 mg/l) (Supplementary Data), *c.* 20 km downstream of the natural Cu mineralization. Also, the mine area waters have lower Zn concentrations (91 $\mu\text{g/l}$) and a significantly higher pH of 7.9 compared to a pH of 5.1 at the end of the Yerba Loca Valley. In the mine area waters of the San Francisco River and the water draining mineralization in the Yerba Loca Stream, the sulphate and nitrate isotope values are almost identical. As discussed previously, the sulphate isotopes reflect the presence of oxidation of sulphides at both localities and the nitrate isotopes an atmospheric origin.

Waters draining the Cu mineralization in the headwaters of the Yerba Loca Stream have higher levels of Cu (11693 $\mu\text{g/l}$), Ni (26 $\mu\text{g/l}$) and Al (6 mg/l) and a lower pH of 2 than *c.* 20 km downstream where values are 4185 $\mu\text{g/l}$ for Cu, 18 $\mu\text{g/l}$ for Ni, 1 mg/l for Al with a pH of 5.1 (Supplementary Data), except for Zn which has a slightly lower value of 124 $\mu\text{g/l}$ than Zn downstream (175 $\mu\text{g/l}$). The anomalously high values of As (14 $\mu\text{g/l}$), Fe (45 mg/l), P (694 $\mu\text{g/l}$) and SO_4^{2-} (446 mg/l) in the Yerba Loca headwaters decrease to background levels over the same distance. This reflects the oxidation of sulphides close to the Cu mineralization and the rapid dilution and precipitation of trace elements such as As that decrease markedly to $<0.5 \mu\text{g/l}$ by the end of the Yerba Loca Valley.

The naturally elevated occurrence of these metals is of high importance in countries rich in metal ores and where industries need to comply with water quality regulation and legislation.

Regional hydrogeochemical data compared with regulation and guideline values

The regional stream water data of Central Chile were compared with the regulation and guideline values for drinking water of Chile, Europe, the US and the WHO (Table 5). Most of the concentrations from Central Chile are below regulation and guideline values, except for SO_4^{2-} in 8.3% of the samples (12 samples), As in 6.9% (10 samples), Hg in 4.8% (7 samples) and Cu in 2% (3 samples) (Tables 1 and 5). The sources of these high values are all natural, with the SO_4^{2-} being derived from evaporites, As and Cu reflecting sulphide mineralization and Hg from hydrothermal alteration. The only exceptions are 3 samples high in Hg that are interpreted to be caused by anthropogenic activity.

Chilean drinking water regulation values have historically followed international guidelines (Table 5), which are of limited value for regulating stream water levels because they do not take into account natural sources of elements derived from the lithology, hydrothermal alteration and mineralization of the rocks they drain. This issue has been considered in the Government and upcoming

environmental legislation will include baseline geochemical requirements and is likely to become mandatory as of 2014 (Townley 2013). The Government draft regulations on surface water quality for the Maipo Basin (CONAMA 2004) were compared to the regional hydrogeochemical data prepared in this study.

The regulation defines the surface water quality for each sub-basin in the Maipo Basin. The regulated levels are defined by calculating the 66th percentile of the data for each sub-basin. However, the sampling sites and dates of data collection are not specified. The values in the regional hydrogeochemical data were found to be well below the stream water regulation levels for most elements, except for Cu and Zn in the headwaters of the Mapocho River and SO_4^{2-} in the headwaters of El Yeso River upstream.

For the Yerba Loca Stream in the headwaters of the Mapocho River, the Cu value of 4185 $\mu\text{g/l}$ is *c.* 300 $\mu\text{g/l}$ higher than the stream water regulation value of 3844 $\mu\text{g/l}$ (CONAMA 2004). This difference may be due to seasonal or annual variation. The highest value above the regulated level is for Zn, which is *c.* 0.2 mg/l in the Yerba Loca Stream and *c.* 0.09 mg/l in the San Francisco Stream, compared to the regulated value of 0.025 mg/l (CONAMA 2004). As the anomalously high value of Zn was interpreted to be related to mineralization in these streams and as the stream water concentrations are generally consistent with the regulation, the difference is believed to be an error in the draft regulation data. This might most likely be a typographical error as the regulated values are based on a report prepared by the Chilean supervisory entity DGA (Dirección General de Aguas) where the value published of 0.25 mg/l Zn for summer for the Yerba Loca Stream (DGA 2004) is consistent with those found in this study *c.* 0.2 mg/l.

For El Yeso, the SO_4^{2-} value of 539 mg/l is *c.* 235 mg/l higher than the draft regulation value of 304 mg/l (CONAMA 2004). This difference may also reflect seasonal or annual variation since the high values of SO_4^{2-} reflect the presence of extensive evaporites in the headwaters.

Conclusions

The regional hydrogeochemical baseline prepared for this research extends over *c.* 20000 km² of Central Chile including the classic copper mining districts of Andina–Los Bronces. Approximately 5000 km² (25% of the area) have highly anomalous concentrations of one or more of the following in stream water: the major cations Ca, Mg, Na, K, Al and Fe; the major anions Cl^- , NO_3^- and SO_4^{2-} ; the trace elements As, Cd, Cu, F, Hg, Mo, Ni, P, Pb and Zn and/or HCO_3^- ; pH and TDS. The sources of the anomalously high levels of elements were identified using trace and major element chemistry and isotope geochemistry based on the geological, land use, field logging of talus and stream float during sampling and the interpretation of Landsat imagery. Within the 5000 km² of affected areas, anomalously high levels extending over *c.* 4000 km² reflect the influence of natural sources comprising bedrock geology (70% of the affected areas, *c.* 3600 km²), hydrothermal alteration (7%, *c.* 380 km²) and Cu-sulphide mineralization (4%, *c.* 190 km²). The remaining *c.* 1000 km² is contamination from anthropogenic sources including fertilizers and sewage (14% of the affected areas, *c.* 710 km²), human settlements (4%, *c.* 200 km²) and mining (1%, *c.* 60 km²).

The major source of natural anomalously high concentrations of elements is from evaporites outcropping in the headwaters of the Maipo River in the Andean Cordillera. The high levels extend downstream and reach the Central Valley. Anomalously high levels of elements in waters draining hydrothermal alteration, for example, in the headwaters of the Colorado River and the Arrayán Stream in the Andean Cordillera are restricted to near the source and are diluted rapidly downstream. Waters draining Cu-mineralized areas such as Barriga River and Yerba Loca Stream also have anomalously high concentrations of elements which occur near the source and are diluted rapidly downstream.

The major anthropogenic source of anomalously high levels of elements is from fertilizers in agricultural areas and sewage from communities in the Central Valley and the Coastal Cordillera. Isotopic compositions of nitrate distinguish nitrate and ammonium-based fertilizers used in agriculture, as well as sewage and mixed sources. Stream waters contaminated by fertilizers occur in tributaries of the Aconcagua River in the Central Valley and in the Maipo River. Stream waters mainly affected by sewage occur in the Mapocho River downstream of Santiago and in the Aconcagua River. Stream waters with mixed agricultural and sewage sources occur in the Coastal Cordillera in the Aconcagua River and some of its tributaries, and in the Central Valley in the Maipo River and some of its tributaries. Stream waters contaminated locally with anomalously high concentrations of Pb or Hg from human settlements occur near seven townships across the region. Water downstream from the ski resorts had locally high values of Al, Fe and P reflecting contamination with household chemicals. Anomalously high levels of elements in the waters proximal to the Andina and Los Bronces mines are thought to be related to waters from mineralization and alteration, which are rapidly diluted downstream to background levels over a distance of *c.* 20 km. The waters draining the abandoned La Poza and Restauradora Pb-Zn mines are highly anomalous in Pb and Zn downstream from the mines.

The waters in the Yerba Loca Valley reflect the oxidation of sulphides close to the Cu mineralization and the rapid dilution and precipitation of most of the trace elements downstream. These waters have significantly higher Cu and Ni levels than the mine area waters in the San Francisco River and a much lower pH. The isotopic composition of the waters indicates the same natural sources of dissolved sulphate and nitrate with no measurable contribution from the use of explosives in the mining districts.

With respect to national and international drinking water guideline values, the majority of concentrations are lower than the stipulated levels with a few exceptions, such as for SO_4^{2-} and As concentrations being derived from natural sources and Hg from both natural and anthropogenic sources.

The majority of the concentrations for the regional hydrogeochemical baseline are below the Chilean draft water quality regulation values for the Maipo Basin. Higher values are related to natural sources including copper sulphide mineralization (Cu, Zn) and evaporites (SO_4^{2-}).

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