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Influence of geomorphological variables on mountainous stream water chemistry (Sierras Pampeanas, Córdoba, Argentina)

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ABSTRACT

The relationship between geomorphological features and water geochemistry was studied for a group of mountainous rivers (from ~900 to ~2200 m a.s.l.) with similar geology and climate, in the Sierras Pampeanas of Córdoba (Argentina, 31° 30′, 32° 00′S, and 64° 30′, 65° 10′W). A multivariate approach was used to identify three morphological domains that describe the set of sampled rivers, namely "size" dominance, slope dominance, and drainage density dominance. The links between physicochemical and geomorphological variables show that "size" dominance is mostly related to major ions, conductivity, and pH, which tend to increase downstream. Slope dominance is associated with the total concentration of heavy metal (i.e., high heavy metal concentrations are associated with relatively flat areas with slightly acid to circumneutral pH, which promotes desorption). The drainage density dominance results in an association between well-drained catchments and low Cl^- concentration (i.e., preserving the chemical signature of atmospheric precipitation).

1. Introduction

Lithology, climate, vegetation cover, and morphology (mostly through relief) have been suggested to be the major factors controlling the yield of rock debris and dissolved solids in drainage basins (e.g., Gibbs, 1970; Garrels and Mackenzie, 1971; White and Blum, 1995; Drever, 1997; Bouchard and Jolicoeur, 2000; Dupré et al., 2003; Riebe et al., 2004; Yuan et al., 2007). Human actions additionally alter the denudation of the land and influence the biogeochemical characteristics of rivers (e.g., Salomons et al., 1995; Soliman et al., 1998; Allen et al., 1998). However, not all the intervening factors have received a comparative share of the attention in the literature. For example, the impact of certain geomorphological aspects (e.g., drainage density as defined by Horton, 1945 and modified by Strahler, 1952) on the biogeochemical character of a specific stream is under-researched.

The UN General Assembly declared the year 2002 as the International Year of the Mountains to direct global awareness to the importance of mountain ecosystems (http://www.unu.edu/mountains2002/index.htm). Mountains were identified by the UN Environment Programme (UNEP) as "the water towers of the world" and, therefore, "vital to all life on earth and to the well-being of people everywhere" (http://www.unep.org). These actions stimulated the initiation of research efforts, such as the Mountain Research Initiative (MRI), *http://mri.scnatweb.ch/*, which seeks to detect signals of global environmental change in mountain environments as well as on the lowland systems that are significantly dependent on adjacent mountainous regions. Therefore, in order to contribute to this ongoing international effort, the effect of quantitatively-defined geomorphological variables on the water chemistry of a set of mountainous rivers and streams that drain the Sierras Pampeanas of Córdoba, Argentina, is explored.

2. Field site

Mountain streams and rivers are those with a slope greater than or equal to 0.2% (Jarrett, 1992; Wohl, 2000). They are responsible for landscape morphology, and for the transport of sediments and solutes released by weathering and denudation (e.g., Drever and Zobrist, 1992; Jacobson et al., 2003; Millot et al., 2002, 2003; Dupré et al., 2003; Brown et al., 2004; Nédeltcheva et al., 2006; Hren et al., 2007; Velbel and Price, 2007). The studied basins occupy a portion of the highest region in the Sierra Grande, one of the major ranges in the Sierras Pampeanas of Córdoba Province in Argentina between 31° 30′ and 32° 00′S and 64° 30′, 65° 10′W (Fig. 1).

Lithology is fairly homogeneous, mainly composed of crystalline rocks: metamorphic rocks (amphibolites and granulite-facies) from the Precambrian basement and granitoids of the Achala Batholith. The amphibolite facies are composed of mica schist, biotitic tonalite gneisses, heterogeneous migmatites, amphibolites, marbles, and quartzite. Granulite-facies rocks are homogeneous migmatites characterized by garnet, cordierite and K-feldspar (Gordillo and Lencinas, 1979). The Achala Batholith is a large granitoid plutonic body (~2500 km^2) emplaced in the range's highest elevation area. Its chemical and mineralogical composition has been extensively studied (e.g., Lira and Kirschbaum, 1990; Demange et al., 1996; Rapela et al., 2008; and references therein). These

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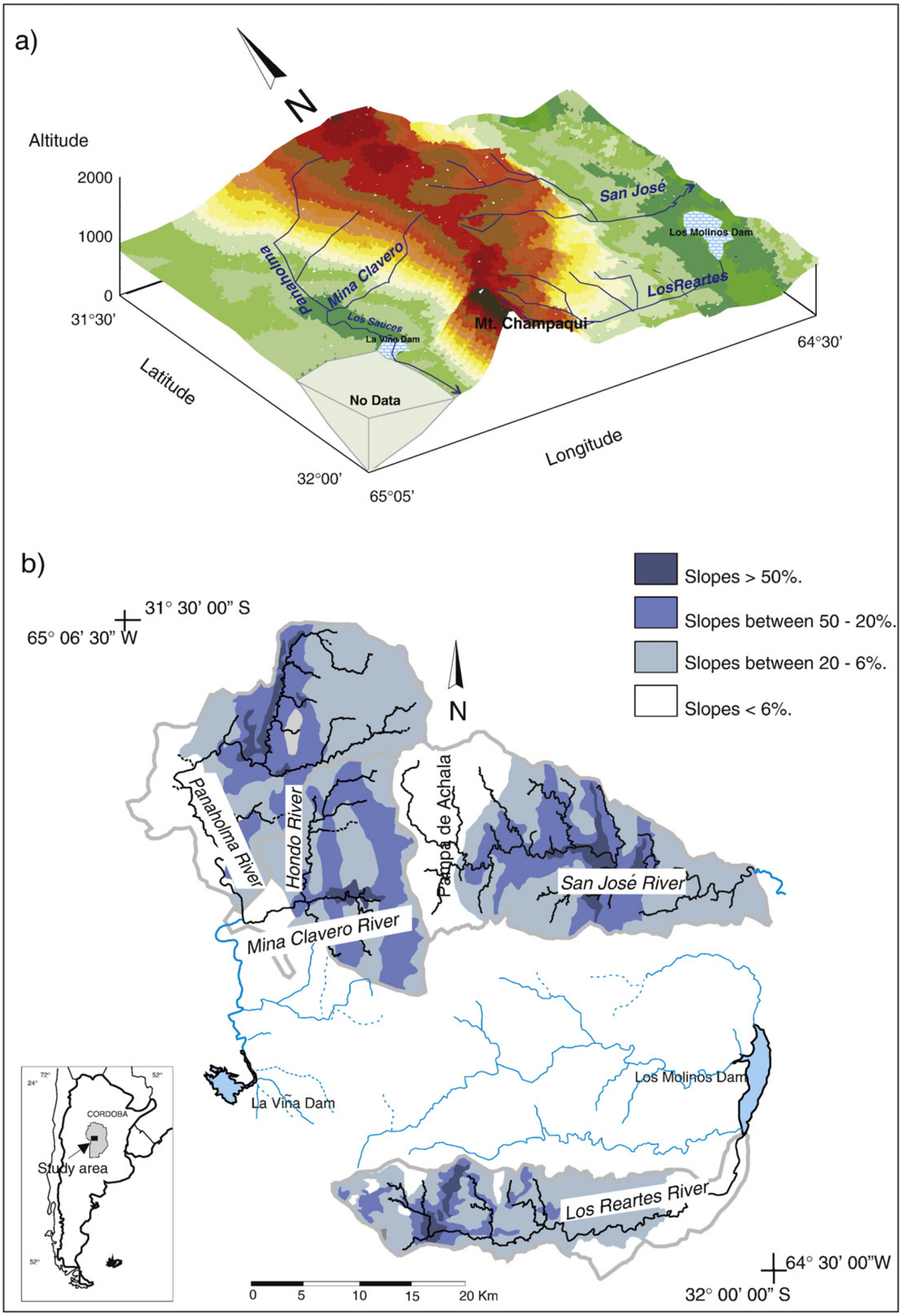

Fig. 1. a) Block diagram showing the general relief in the study area (Sierras Pampeanas of Córdoba, Argentina); b) schematic map of the same area, indicating basin slopes. The on-line version is colored; shades of gray are used in the paper version.

granitoids are calc–alkaline and peraluminous, mainly composed of biotitic granite and biotitic–muscovite granite facies. The main mineralogy is quartz, plagioclase (An_{2-22}), microcline, muscovite and biotite. Accessory minerals present in the granitoids are fluorapatite, apatite, zircon, magnetite–ilmenite, rutile, titanite, chlorite, kaolinite and uraniferous minerals. Very limited fluvial (autochthonous) and loess-like sediments (allochthonous) are present in the highest part of the batholith. The soil is patchy and immature.

The present day Sierra Grande resulted from the uplift on a reverse fault during an upper Tertiary stage of the Andean orogeny and planation is mainly responsible for the relict high plain, known as Pampa de Achala (Carignano et al., 1999), that extends for several hundreds of kilometers. Steeper slopes are found on the range's western side, reaching mean values of about 10%, whereas gradients are lower on the eastern side, with values of approximately 5% (Fig. 1).

Climate in the mountainous study area is sub-humid to semi-arid. A temperate regime, irregular rainfall concentrated in one season (summer), and occasional snowfall in winter are typical features. About 80% of the annual rainfall occurs between October and April, with values higher than 50 mm per month. Annual average precipitation increases from 600 mm in the eastern lowlands to more than 1000 mm in the Pampa de Achala region. On the western slope, annual rainfall is lower, ranging between 500 and 800 mm. The mean annual temperature in the area is 16 °C, decreasing to 10 °C at about 2000 m a.s.l. (Vazquez et al., 1979).

The climatic and tectonic characteristics of the area have produced a weathering-limited environment where transport processes that remove weathered material (mechanical erosion) are faster than the processes generating mineral debris (Stallard and Edmond, 1983). Weathering is highly selective; i.e. only the most reactive minerals contribute to the solute load while less reactive minerals are transported away by physical erosion (White, 2005).

The four selected rivers, Panaholma, Mina Clavero, Los Reartes and San José, are characterized by slopes that vary between ~4 and ~9%. They cover a large region where the other environmental variables (i.e., lithology, climate, vegetation) are similar. The confluence of the Mina Clavero and Panaholma rivers forms the Los Sauces River that flows to the Sierra Grande's western side (i.e., steeper slope), and discharges into the La Viña reservoir. Los Reartes and San José rivers drain on the eastern and less steep side of the Sierra Grande and are part of the Xanaes River drainage basin (Fig. 1).

Streams and rivers in the four studied drainage basins consist of first to fifth order streams, according to Horton's (1945) classification as modified by Strahler (1952).

Landscapes units with similar combinations of climate, soil, and vegetation, and hence similar hydrological and water balance behavior are called hydrotopes (Becker, 2005). In the study area, we have determined that the most ubiquitous hydrotope is the ASL type (i.e., slope areas with potential overland flow and interflow). The headwaters that flow on exposed bedrock correspond to the AIMP hydrotope type (i.e., impervious areas), while areas with shallow groundwater table are of the AN hydrotope type.

3. Methods

3.1. Sampling and analysis

Eighty-one samples of surface waters were collected from the four studied mountainous drainage basins to obtain information on the chemical signal of solutes. The criterion employed in the selection of the study area was its relative freedom from direct anthropogenic influence. Being the uppermost part of the mountainous range, this area is relatively free from inhabitants, cattle, or crops. We tried to sample all the represented stream orders, as long as sampling sites were accesible. Samples were collected in main channels, tributary streams and spring waters from 28 sampling points. To compensate for the effect of the irregular seasonal atmospheric precipitation distribution, samples were taken at 3 different times: December 2003, May and November 2004. For statistical analysis, means were used so as to avoid the excessive weight of seasonality and in order to bring forward the control exerted by geomorphology.

Water temperature, pH, electrical conductivity, and alkalinity were measured *in situ*. Alkalinity was measured as the concentration of $CaCO_3$ using a 0.1600 N H_2SO_4 titration and an end point of pH = 5.1 in unfiltered water. For subsequent determinations, samples were vacuum-filtered in the field with 0.22-μm pore-size cellulose filters (HA-type, Millipore Corp.) and divided into two aliquots. One aliquot was acidified (pH<2) with concentrated and redistilled (≥99.999%) HNO_3 (Aldrich Chemical Co.) for the analytical determination of major, minor, and trace elements by inductively coupled plasma-mass spectrometry (ICP-MS, Activation Laboratories Ltd., Ancaster, Ontario, Canada). The other aliquot was stored in polyethylene bottles at 4 °C for the measurement of anion concentrations by chemically suppressed ion chromatography with conductivity detection. For most of the analyzed stream waters, the charge imbalance between cations and anions was less than 5%.

Table 1
Main geomorphological characteristics of the four analyzed drainage basins.

Drainage basin	San José	Los Reartes	Panaholma	Mina Clavero
Slope	Eastern	Eastern	Western	Western
Stream order	5	5	5	5
Mean slope (%)	5.9	4.4	5.9	9.2
Area (km^2)	427	203	323	198
Perimeter (km)	82	79	86	66
N° of 1st order streams	533	141	310	128
Mean 1st order lenght (km)	0.62	0.58	0.68	0.81
TLCh (km)	673	211	451	229
TNCh	702	196	404	182
DD (m km^{-2})	1.58	1.04	1.39	1.16
DF (n° km^{-2})	1.64	0.97	1.25	0.92
Stream-lengh ratio	3.38	3.08	2.95	2.45
Bifurcation ratio	4.84	3.46	4.31	3.39

TLCh: total length of channels; TNCh: total number of channels; DD: drainage density; DF: drainage frequency.

The results for major, minor and trace elements were validated using NIST (National Institute of Standards and Technology) 1640 and Riverine Water Reference Materials for Trace Metals certified by the National Research Council of Canada (SRLS-4) control material. To check reproducibility of results, replicated analyses were conducted on several samples (1G18-MC, 2K9-PH, 2K27-LR, 3K12-PH and 3K23-MC). Measuring errors were less than 10% for major and minor elements. Lower concentrations, as in the case of trace elements, produced higher analytical uncertainty.

3.2. Geomorphological variables and multivariate statistical analyses

The geomorphological characterization of the basin was performed following the methodology proposed by Horton (1945), and modified by Strahler (1952) (Tables 1 and 2). Areas and lengths were measured using ArcView GIS. Area values were corrected according to the measured slope angles so as to represent real area, not projected surfaces. Other geomorphological variables (slope, stream order, number of 1st order streams and total number of channels) were calculated from topographic charts (1:50,000).

Before performing statistical analyses, geomorphological and physicochemical data were transformed to their logarithms whenever necessary in order to achieve univariate normality. These matrices were used as the basic input database (Table 2).

Unrotated factor analysis (Davis, 1986) was undertaken using the database that is summarized in Table 2 (15 variables). Drainage frequency was excluded because it is directly correlated with drainage density and would therefore mask other results. This analysis combines numerous variables into some independent variables as principal components, which explain — in a statistically significant way — the greatest amount of variation of the multivariate data.

4. Results and discussion

4.1. Geomorphological setting

A stream system in a drainage basin can be expressed quantitatively in terms of stream order, area, drainage frequency (i.e., the ratio of total number of channels to basin area), drainage density (i.e., the ratio of total river length to basin area) and slope, amongst other

Table 2
Mean values; ± standard deviation of variables in the four analyzed drainage basins.

Samples	pH	Conduct.	TDS	Alkalinity	ΣCations	$Cl^- + SO_4^{2-}$	ΣTransition metals	ΣREE	Slope	Area	Perimeter	TLCh	TNCh	DD	Elevation
		μS cm^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	μg l^{-1}	μg l^{-1}	m m^{-1}	km^2	km	km		m km^{-2}	m
San José River															
1 –2° order	7.4 ± 0.7	53.6 ± 15.3	48.5 ± 13.8	18.6 ± 8,3	12.7 ± 4,13	7.6 ± 2.0	560.0 ± 859	1.9 ± 2,92	0.06 ± 0.05	3.4 ± 2.5	6.2 ± 4.0	5.4 ± 4.2	6 ± 5.6	1.4 ± 0.3	1890 ± 383
3°–4° order	7.6 ± 0.7	52.8 ± 14,4	48.1 ± 7.5	15.1 ± 5,8	11.7 ± 3,16	6.5 ± 0.8	188.7 ± 122	0.9 ± 0,81	0.03 ± 0.00	24.4 ± 14.5	18.3 ± 7.8	39.4 ± 24.3	41 ± 26.6	1.6 ± 0.1	2065 ± 21
5° order	7.0 ± 0.9	53.6 ± 13,1	35.9 ± 1.3	16.2 ± 5,2	9.4 ± 2,04	6.4 ± 1.4	98.0 ± 19,4	0.7 ± 0,28	0.06 –	427.3 –	76.2 –	563.2 -	685 -	1.3 -	913 -
Mina Clavero River															
1°–2° order	7.1 ± 0.5	44.4 ± 17,9	41.9 ± 12.9	14.7 ± 7,5	10.1 ± 3,92	7.4 ± 2.5	163.3 ± 137	0.7 ± 0,45	0.30 ± 0.37	2.0 ± 2.1	3.4 ± 3.1	1.9 ± 2.6	1.7 ± 1.2	0.7 ± 0.4	1476 ± 291
3°–4° order	7.5 ± 0.6	42.6 ± 8,6	40.0 ± 7.1	15.6 ± 4,6	8.9 ± 1,75	5.8 ± 1.3	107.4 ± 65,7	0.3 ± 0,25	0.09 ± 0.03	7.7 ± 7.2	10.2 ± 3.8	12.6 ± 8.6	17 ± 11.4	1.9 ± 0.8	1678 ± 143
5° order	7.2 ± 0.1	64.6 ± 14,5	47.7 ± 13.5	17.2 ± 6,5	13.7 ± 3,26	11.1 ± 4.3	99.4 ± 59,8	0.6 ± 0,25	0.09 -	198.1 ± 0.0	66.5 ± 0.0	228.6 ± 0.0	182 ± -	1.2 -	993 -
Los Reartes River															
1°–2° order															
3°–4° order	7.4 ± 0.4	37.2 ± 7,2	40.5 ± 10.5	22.0 ± 11,6	7.9 ± 1,18	4.7 ± 2.7	44.6 ± 22,3	0.3 ± 0,09	0.10 -	50.3 -	30.0 -	68.5 -	63 -	1.4 -	1270 -
5° order	7.9 ± 0.3	78.3 ± 28,2	55.9 ± 14.7	38.0 ± 16,7	16.3 ± 5,54	7.5 ± 2.5	59.8 ± 36,7	0.3 ± 0,22	0.06 ± 0.01	161.6 ± 45.4	64.5 ± 15.9	185.5 ± 19.2	192 ± 6.4	1.2 ± 0.2	919 ± 128
Panaholma River															
1°–2° order	6.6 ± 0.8	47.0 ± 25,6	33.9 ± 15.1	9.9 ± 7,2	8.2 ± 4,43	7.1 ± 4.0	122.9 ± 52,8	0.7 ± 0,27	0.12 ± 0.14	0.8 ± 0.8	2.7 ± 1.3	1.0 ± 0.8	1 ± 0.0	1.2 ± 0.6	1894 ± 346
3°–4° order	7.5 ± 0.4	72.0 ± 23.5	54.1 ± 16.2	26.4 ± 12,1	15.2 ± 6,40	8.4 ± 2.6	142.2 ± 160	0.6 ± 0,67	0.07 ± 0.01	47.6 ± 29.9	29.7 ± 10.7	91.6 ± 63.2	111 ± 0.5	1.8 ± 0.3	1044 ± 82
5° order	8.1 ± 0.3	202 ± 168,4	96.9 ± 61.4	66.7 ± 45,9	37.0 ± 30,1	27.6 ± 33.8	68.9 ± 53,9	0.3 ± 0,32	0.06 ± 0.01	231.2 ± 77.8	64.6 ± 17.8	370.6 ± 68.1	351 ± 0.4	1.7 ± 0.2	1013 ± 35

$N = 28$ for geomorphological variables, and $N = 81$ for geochemical variablesTLCh: total length of channels; TNCh: total number of channels; DD: drainage density.

variables (Horton, 1945; Strahler, 1952). These quantitative geomorphological parameters were measured and calculated for each of the four drainage basins (San José, Mina Clavero, Los Reartes and Panaholma drainage basins, Table 1) and amongst other variables for each sampling station, from the water divide downstream to the corresponding sampling point (Table 2).

The analysis of morphological features clearly shows that drainage nets exhibit a dendritic design that is controlled by the abundant geological joints. All four drainage basins have a Strahler order of five; area values vary from ~200 to >400 km^2. The drainage frequencies of the basins are low (between ~0.9 and ~1.6 channels km^{-2}), as are drainage densities, ranging between ~1 and ~1.5 km km^{-2}. The highest area (e.g., Pampa de Achala at 2000 m a.s.l.) is relatively flat, with slopes <6%. As mentioned above, western basins present steeper slopes than the eastern ones.

We followed the approach of Thompson et al. (2006), which characterizes the reaches in a catchment according to the relationship between area and slope. Points in the scatter plot in Fig. 2 correspond to the relationship between area and slope calculated for each sampling station reach. In general, uppermost reaches correspond to the cascade and steep-pool reach types. An exception is the uppermost San José drainage basin in the Pampa de Achala, which is the flattest relief-type in the region and where the planebed reach predominates. Some spring-fed streams that flow though bare rock plot within the bedrock type field.

Moreover, 4th and 5th order rivers (i.e., the lowermost fluvial reaches) classify as both, the bedrock and planebed types. The first type, encompassed those reaches with a typical ravine morphology, where steep sides inhibit sediment accumulation. Planebed reaches allow the accumulation of sediment, where a larger sediment specific surface area and a longer residence time favor chemical reactions. Notice that there are no slopes with less than 0.01 m m^{-1} (i.e., pool-riffle type) (Fig. 2).

4.2. The solute chemistry

Stream waters were generally found to be diluted, with total dissolved solids (TDS) concentrations that range between 9.6 and 70.6 mg l^{-1}. There are, however, some outliers with relatively high TDS concentrations (over 240 mg l^{-1}) that reflect inputs from colluvium accumulated on gentle slopes. At the time of sampling, stream water temperature ranged between ~4 °C (i.e., snow fell during the second sampling interval) and ~29 °C in the last sampling performed in summer. These samples showed acid to alkaline pH (5.6 as in snow to 8.8 in stream water). In general, in the studied region, pHs in the acid range are associated with precipitation dominance while alkaline pHs are determined by mineral weathering.

Table 2 shows arithmetic mean values of physicochemical and morphological characteristics and their corresponding standard deviations. It also shows the total concentrations of transition metals (i.e., the added concentration of dissolved Fe, Ti, Mn, Zn, V, Cr, Cu, Ni, Sc, and Co) and rare earth elements (REE, i.e., La to Lu).

The analysis of physicochemical parameters (with the exception of transition metals and REE) in the headwaters of each catchment (Table 2) shows similar orders of magnitude and restricted variation for most variables, suggesting the strong influence of precipitation (e.g., $Cl^- + SO_4^{2-} \approx 7$ mg l^{-1}; conductivity fluctuates between 40 and 50 μS cm^{-1}; pH varies between 6.6 and 7.4). The downstream chemical variation in Los Reartes and Panaholma rivers exhibit a significant increase in the value of every variable (i.e., pH, conductivity, TDS, alkalinity and major ions), due to the occurrence of metamorphic or sedimentary lithology in their lowermost reaches. Both rock types exhibit, in general, a larger specific area and, hence, are more likely to supply solutes than igneous rocks do. In contrast, both the Mina Clavero and the San José drainage basins exhibit little lithological variation. The change in all the above mentioned variables

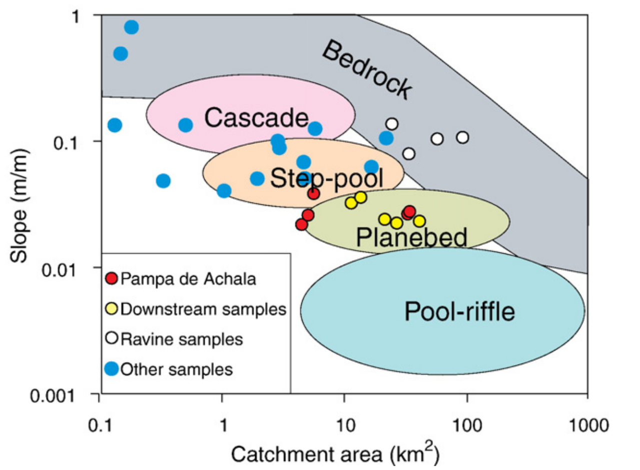

Fig. 2. Scatter diagram showing the relationship between slope and the reach area upstream of each sampling point (modified from Thompson et al., 2006). The graph separates the San José River uppermost samples (Pampa de Achala), the lower reaches (downstream samples), and ravine samples from the remaining sample set.

in the Mina Clavero River is less noticeable, while San José River exhibit a slight concentration decrease in the downstream direction (e.g., cations and anions, pH, TDS), probably due to dilution and/or adsorption.

Samples are, according to Piper's water classification (1944), of the Na^+–K^+ to Ca^{2+}-type, and SO_4^{2-} to HCO_3^--type (Fig. 3). Shadowed areas in Fig. 3 show the chemical variability imposed on the region by atmospheric precipitation. Snow and rainwater are known to contain variable concentrations of solutes, which are mostly supplied by the dissolution of particles in the atmosphere. The nature of atmospheric particles is highly variable as they may be supplied by natural sources, human activities, or formed by atmospheric reactions. Elements that are usually supplied by natural sources are Na, I, Al, K, Cl, Ti, and Fe. Some other elements are largely supplied by human activities, such as Cu, Mn, Zn, Pb, Cd, etc. Finally, some components are formed by atmospheric reactions such as NO_3^-, NH_4^+, SO_4^{2-}, SO_2, etc (e.g., Manahan, 1994). Wet precipitation in the study area is known to supply important amount of REE (García et al., 2007) but its contribution to the major ion pools in river water is rather limited. In consequence, the source of major ions in surface water is mainly mineral weathering. The variation of major chemical components is discernible in the graph: in the upper drainage basins, water is of the SO_4^{2-}–Na^+–K^+-type, with a significant overlap with the chemical composition of rainfall and snowfall. Downstream, HCO_3^-–Ca^{2+} becomes the dominant type. This is controlled by weathering that consumes CO_2 and liberates HCO_3^- in the hydrolysis of silicates that have $Ca^{2+}>Na^+$ content.

Lecomte et al. (2005) analyzed and quantified weathering in the Los Reartes drainage basin through PHREEQC modeling (Parkhurst, 1995). They showed that the processes occurring in the catchment are: the dissolution of plagioclase, calcite, muscovite, and biotite; the precipitation of illite and kaolinite; and a significant consumption of CO_2 by weathering reactions. Between 10^{-3} and 10^{-1} mmol kg^{-1} H_2O of different phases are dissolved or precipitated in the reactions.

In order to analyze chemical weathering in the region, we plotted samples in scatter diagrams of anions and cations. In the absence of halite, which is normally the case, Cl^- in water is mostly supplied by precipitation. Ca^{2+} and SO_4^{2-} are provided mainly by the dissolution of gypsum, which may be wind-transported from nearby Salinas Grandes or present in outcropping sediments. Scatter diagrams representing halite and gypsum mineral dissolutions show that the cations originating from both these minerals are more concentrated than the theoretical stoichiometric relationship (i.e., 1:1 molar correspondence), suggesting that dissolved chemistry in surface waters is not only controlled by atmospheric input or dissolution of evaporites, but also by other sources for Na^+ and Ca^{2+}, such as rock weathering. Concordantly, high bivariate relationships between HCO_3^- and alkaline cations suggest silicate solute sources (plagioclase, feldspar, and mica) and carbonate weathering. In order to confirm possible sources of dissolved elements, we also plotted samples in the

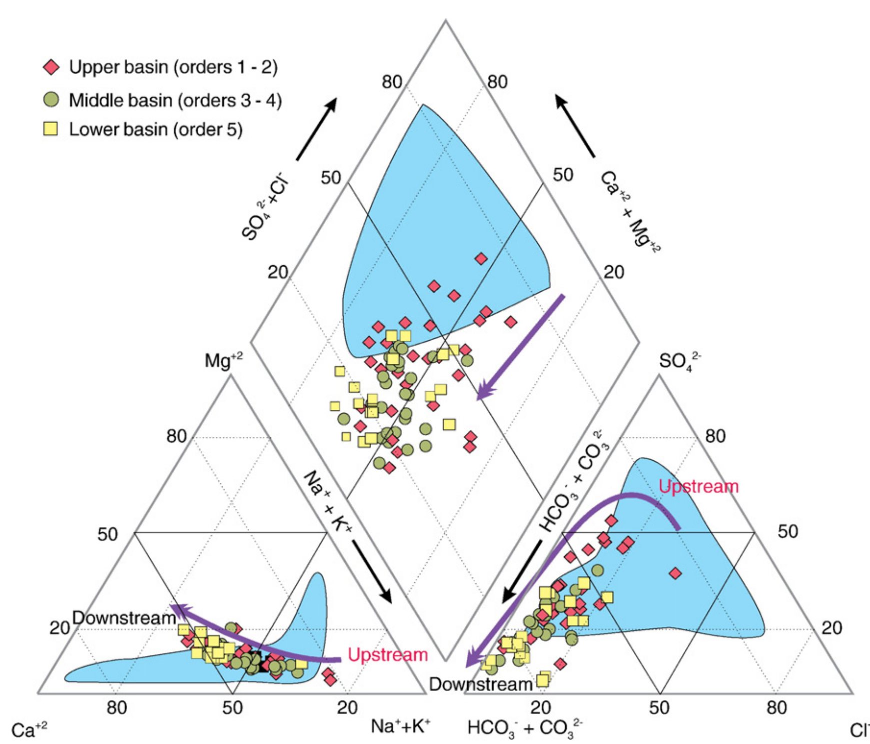

Fig. 3. Piper's (1944) diagram showing the major ion chemistry of sampled rivers. Arrows indicate the chemical variation in the downstream direction. Shadowed areas correspond to the regional chemical variability of atmospheric wet precipitation.

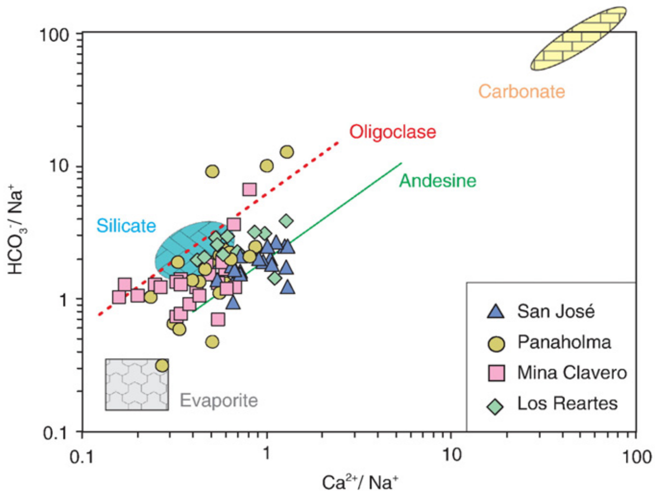

Fig. 4. Scatter graph showing likely solute sources in the studied river systems. Notice that plotted points mainly fall within the boundaries defined by oligoclase and andesine composition. The main drainage basins are identified in the legend box.

diagram in Fig. 4 modified from Gaillardet et al. (1999). This diagram shows the end members of silicate, carbonate or evaporite hydrolysis/dissolution. Fig. 4 shows a concentration of samples around the ideal silicate source, revealing that ions are liberated into water by the weathering of such minerals. As an example, the theoretical dissolution segments for andesine and oligoclase, which are the dominant plagioclases in the region, are plotted in Fig. 4. Subtle differences (not statistically significant) between the basins may be attibutable to minor lithologic variation.

Finally, REE and transition metals present a contrasting behavior to major elements because they tend to decrease significantly downstream. Pasquini et al. (2004) proposed that the concentration of dissolved REE in Los Reartes River drainage basin was controlled by water pH and by adsorption processes that explain the downstream decrease in K_d values $[(\mathrm{REE})_{\text{-water}}/(\mathrm{REE})_{\text{riverbed sediment}}]$. Moreover, García et al. (2007) explained the behavior of REE in the Sierras Pampeanas of Córdoba, reflecting the balance between the REE input from precipitation and their removal by adsorption. They concluded that steep slopes and semi-arid conditions are responsible for the low rates of chemical weathering, so that most of the dissolved REE pool must be delivered by atmospheric precipitation.

4.3. Influence of morphological aspects on dissolved chemistry

Univariate and multivariate statistical analyses were utilized to characterize relationships between variables. As an initial approach, to probe the influence of morphological variables on the geochemistry of natural waters, factor analysis (unrotated) was performed to detect the structure in the relationships between variables. The result of this analysis indicated three principal components which explained ~80% of the total sample variance. Factor loadings captured 51%, 19% and 11% of the total variability, respectively.

Table 3 shows factor loadings with their corresponding communalities. We interpreted factor 1 as a "size factor" (PC-*size*), involving morphologic variables that are controlled by size–shape parameters (area, perimeter, total length of channels, total number of stream channel, and elevation) and it includes physicochemical variables such as conductivity, TDS, cation concentration, alkalinity and pH. With the exception of elevation, loading coefficients are positive, indicating a direct relationship between them. The PC-*size* factor controls major element concentrations and these affect conductivity or TDS and pH values. When geomorphological variables (corresponding to this principal component) have high values or they increase downstream, the water residence time in the catchment is enhanced, thus favoring dissolution or silicate hydrolysis.

An interesting feature is elevation. It showed a negative correlation with those physicochemical variables that exhibit a positive correlation with "size" variables. However, both REE and transition metals show a contrasting behavior to that described above, because their concentrations tend to decrease downstream due to their sequestration through adsorption or to dilution processes, as discussed previously.

Loading coefficients indicate that weighty samples in the PC-*size* factor are those that have high and positive scores, and they belong to the lower reaches of the basins (i.e., samples from the lowermost stretch of Panaholma River, like K9-PH, K11-PH, K25-LR, and K28-PH, Fig. 5). Moreover, those samples with contrasting features (i.e., low values in the associated variables, high elevation and negative scores), also exhibit significant weight (i.e., samples from the uppermost basin of Panaholma River, as K7-PH, K8-PH, and K19-PH, shown with underlined labels in Fig. 5).

The second extracted factor represents the control exerted by the slope on the concentration of transition metals (PC-*slope*) and they are the only variables that have a significant loading in this factor. In this case, coefficients have opposite signs: slope has a negative loading whereas transition metals have a positive coefficient, thus indicating an inverse relationship between them. Those samples collected in steep river reaches that exhibit low dissolved metal concentration are the ones which supply a significant value in the associated factor score matrix, and correspond to samples K20-MC, K21-MC, and K27-LR representing upper basins (Fig. 5). The opposite is also true: gentle slope rivers tend to show increased concentrations of transition metals and are represented by Pampa de Achala samples, as in K2-SJ, K3-SJ, K4-SJ, and K5-SJ, again shown with underlined labels in Fig. 5. These conclusions were also reached by Lecomte et al. (2005), who evaluated the effect of relief by analyzing the output of inverse geochemical models in two sectors with contrasting slopes and outcropping metamorphic rocks. In this manner they addressed the significance of the general slope of the terrain on the production of solutes by leaving fixed lithology and rainfall.

Finally, factor 3 (PC-*dd*) accounts for 11% of the total variance and underlines the significance of two variables: drainage density and dissolved Cl^- concentration. They are inversely correlated: drainage density has a positive coefficient whereas Cl^- has a negative one. This indicates that factor 3 highlights samples with low Cl^- concentration and high drainage density. The negative association is probably determined by the fact that well-drained catchments tend to preserve

Table 3
Factor analysis of all considered variables.

	Factor 1 (PC-*size*)	Factor 2 (PC-*slope*)	Factor 3 (PC-*dd*)	Communalities
pH	**0.76**	0.28	0.02	0.66
Conductivity	**0.81**	0.43	-0.20	0.89
TDS	**0.74**	0.61	-0.02	0.91
Alkalinity	**0.87**	0.25	-0.02	0.83
Cations	**0.78**	0.55	-0.13	0.93
Chloride	0.42	-0.04	**-0.74**	0.73
Transition metals	-0.45	**0.77**	0.20	0.83
REE	-0.51	0.56	0.07	0.57
Slope	0.09	**-0.81**	-0.09	0.67
Area	**0.92**	-0.16	0.11	0.89
Perimeter	**0.91**	-0.18	0.21	0.90
TLCh	**0.91**	-0.17	0.28	0.93
TNCh	**0.88**	-0.19	0.26	0.88
DD	0.20	-0.10	**0.84**	0.75
Elevation	**-0.75**	0.39	0.30	0.81
Explained variability	7.69	2.85	1.65	**12.19**
% expl. Variability	**51.29**	**18.99**	**10.98**	**81.25**

Unrotated factor loadings. Bold loadings are >0.70.
TLCh: total length of channels; TNCh: total number of channels; DD: drainage density.

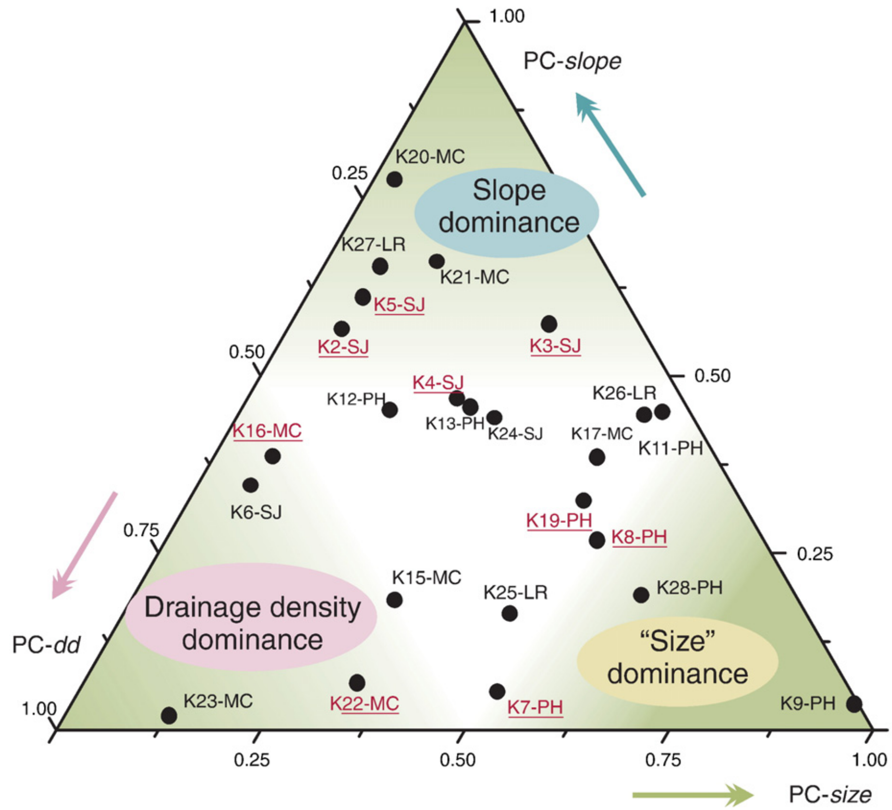

Fig. 5. Normalized ternary diagram with sample distribution according to their respective positive and negative (with underlined labels) factor scores. See text for additional information.

the Cl^- signature of rainfall. The PC-*dd* factor is described, in general, by samples from the upper Mina Clavero drainage basin, such as K16-MC and K22-MC (shown with underlined labels in Fig. 5), and K15-MC and K23-MC.

Communalities (Table 3) indicate the percentage of each variable explained by the three factors. It is evident that REE variability is poorly accounted for by these factors (<0.60) because, as mentioned above, they are controlled by others parameters (García et al., 2007, and references therein). Four variables show communalities >0.90: cations, TDS, perimeter, and total length of channels.

5. Concluding comments

The results obtained in our study on the effect that geomorphologic characteristics have on the behavior of physicochemical variables in mountainous river waters, show that:

a) all physicochemical variables which are statistically correlated with the size of the catchments and, hence, with the water–rock debris contact area, tend to increase in the downstream direction (e.g., conductivity, major ion concentrations, pH);
b) slope controls the time after the occurrence of precipitation events, that water remains in the drainage system. This appears to have a direct effect on the concentration of trace metals, which may be sequestered from solution by adsorption mechanisms, provided that the time of sediment-water contact is sufficiently large. Contrastingly, flat slopes (as in Pampa de Achala) tend to have an acidic to circumneutral pH that favors desorption and hence, such streams have an increased heavy metal concentration; and
c) well-drained catchments at high elevations tend to exhibit low Cl^- concentrations. It is plausible that such areas preserve the Cl^- signature of atmospheric precipitation.

The geochemistry of dissolved elements in mountainous rivers, besides being affected by climatic characteristics and lithology, are also indirectly controlled by the dominant geomorphology, which affect the water residence–time in the catchments and the extension of rock–water contact. Future research should focus further on the study of the factors affecting river water geochemistry in drainage basins with comparable lithology and climate, so as to increase our knowledge on the feedback effect of geomorphology on riverine geochemical dynamics over short time and length scales.

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