



## Hydrochemical characterization of water resources in the Santa María Valley, NW of Argentina

Sales A.<sup>1\*</sup>, López J.P.<sup>2</sup>, García J.<sup>2</sup>, Balverdi P.<sup>1,3</sup> and Marchisio P.<sup>1</sup>

<sup>1</sup>Instituto de Química Analítica, Facultad de Bioquímica, Química y Farmacia. Universidad Nacional de Tucumán. Ayacucho 471. S. M. de Tucumán. CP 4000, Argentina

<sup>2</sup>Facultad de Ciencias Naturales, Universidad Nacional de Tucumán, Miguel Lillo 205. S. M. de Tucumán. CP 4000. Argentina

<sup>3</sup>CONICET, Consejo Nacional de Investigaciones Científicas y Técnicas, Rivadavia 1971, CI 033 AAJ, Buenos Aires, Argentina  
amsales00@gmail.com

Available online at: [www.isca.in](http://www.isca.in), [www.isca.me](http://www.isca.me)

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### Abstract

*Hydrochemical researches in Santa María Valley located in Catamarca and Tucumán in the northwest of Argentina were carried out to assess the chemical characteristics of surface water and groundwater, to understand the sources of dissolved ions by defining the principal hydrochemical processes in order to provide theoretical bases to developing strategies of natural resources uses in the region. This region is dominated by a semi-arid climate. A total of twenty five water samples have been collected. The physicochemical parameters determined in water by standardized methods were pH, electrical conductivity (EC), major ions (calcium, magnesium, sodium, potassium, chloride, sulphate, carbonate and bicarbonate) and Total Dissolved Solids (TDS). According to the Piper diagram, the region mainly contains Na-Ca-HCO<sub>3</sub> followed by Na-HCO<sub>3</sub>-Cl, Ca-Na-HCO<sub>3</sub>-SO<sub>4</sub> and Mg-Ca-Na-HCO<sub>3</sub> water types. The contents of sodium, calcium, magnesium, chloride, sulphate and bicarbonate in the waters of the area are explained by the dissolution of halite, calcite, dolomite and gypsum and other reactions like cation exchange and weathering of minerals of basement rocks.*

**Keywords:** Hydrochemistry, Groundwater, Surface Water, Arid zones, Argentina.

### Introduction

A better understanding of hydrochemical systems in arid regions can contribute to an effective management and utilization of natural resources by clearly stating the relationship among water chemical composition, aquifer lithology and recharge type<sup>1-4</sup>. The main source of water for human consumption, agricultural and industrial uses in many countries proceeds from the groundwater. The government and scientist have performed studies of water resources.

The Valley of Santa María River, with a length of more than 100 km north-south, is located in the northwest of Argentina, from Punta de Balasto in the province of Catamarca, to the north of Cafayate in the province of Salta (Figure-1). On the studied area, the hydrogeochemical studies are scarce. Some authors spread hydrological data of the region<sup>5,6</sup>. The zone of hydrogeological value is confined to the most depressed part of the valley, a 4 km wide area of about 160 Km<sup>2</sup>, that provides groundwater for domestic and agricultural uses in this region. Groundwater is the most important source of water supply in the Valley of Santa María due to its intense agricultural activities. The region has significant reservoirs of groundwater and geophysical studies allowed determining the most favorable areas for their exploitation and highlighted the importance of the basin filled with rivers and streams that flow down from the high peaks.

The geochemical processes that take place in the natural waters change spatially and temporally, according to the rock composition and chemical characteristics of the aquifer<sup>7</sup>. The chemical composition of natural waters is controlled by many factors that include soluble products of rock weathering and decomposition, geological structure, mineralogy of watersheds and aquifers and geological processes inside the aquifer.

The geochemical evolution of groundwater is related to various factors such as the direction of regional flow, the mineralogical composition of the aquifer materials and the residence time of water in them. The water is mineralized, while flowing, after long periods of time in contact with geological formations. Several reactions like dissolution, precipitation, ionic exchange, etc. can be produced. The weathering of minerals produces the release of cations and silica<sup>8-10</sup>.

The study of the ion ratios in the waters allows defining the chemical processes (dissolution - precipitation, oxidation - reduction, ion exchange) that determine water composition<sup>11</sup>.

Under normal conditions, the ionic type of water changes from bicarbonate-calcium in low depth aquifers and in recharge zone into sulphate-calcium-sodium in intermediate depth aquifers and in conduction areas to finally turns into chloride-sodium in deep aquifers and discharge areas. Nevertheless, these normal conditions are altered in nature by the presence of geological

formations with soluble salts (limestone, gypsum, dolomite, halite) that produce premature salinization of natural water. On the other hand, igneous and metamorphic rocks and their sedimentary products (sands and gravels) have low mineralization waters. For all these reasons, the interpretation of water chemical analysis from a given area provides information about spatiotemporal ionic variations, underground flow direction and mineralogical composition of the lithological substratum.

The groundwater chemical characteristics in semiarid regions are controlled by different types of reactions like dissolution or weathering of minerals and cation exchange<sup>1</sup>. Some authors suggest that two types of hydrogeochemical processes are very

important: cation exchange and the calcite equilibrium<sup>12</sup>. Others authors propose that the principal processes are carbonate dissolution, halite dissolution, Ca/Na ion exchange, and Mg/Na ion exchange<sup>13</sup>. Besides, gypsum dissolution and illite precipitation/dissolution are also responsible for the chemistry of groundwater<sup>14</sup>.

The aim of this work was to determine the chemical characteristics of surface water and groundwater in the Valley of Santa María in the northwest of Argentina by defining the principal hydrochemical processes in order to provide theoretical bases to developing strategies of natural resources uses in the region.

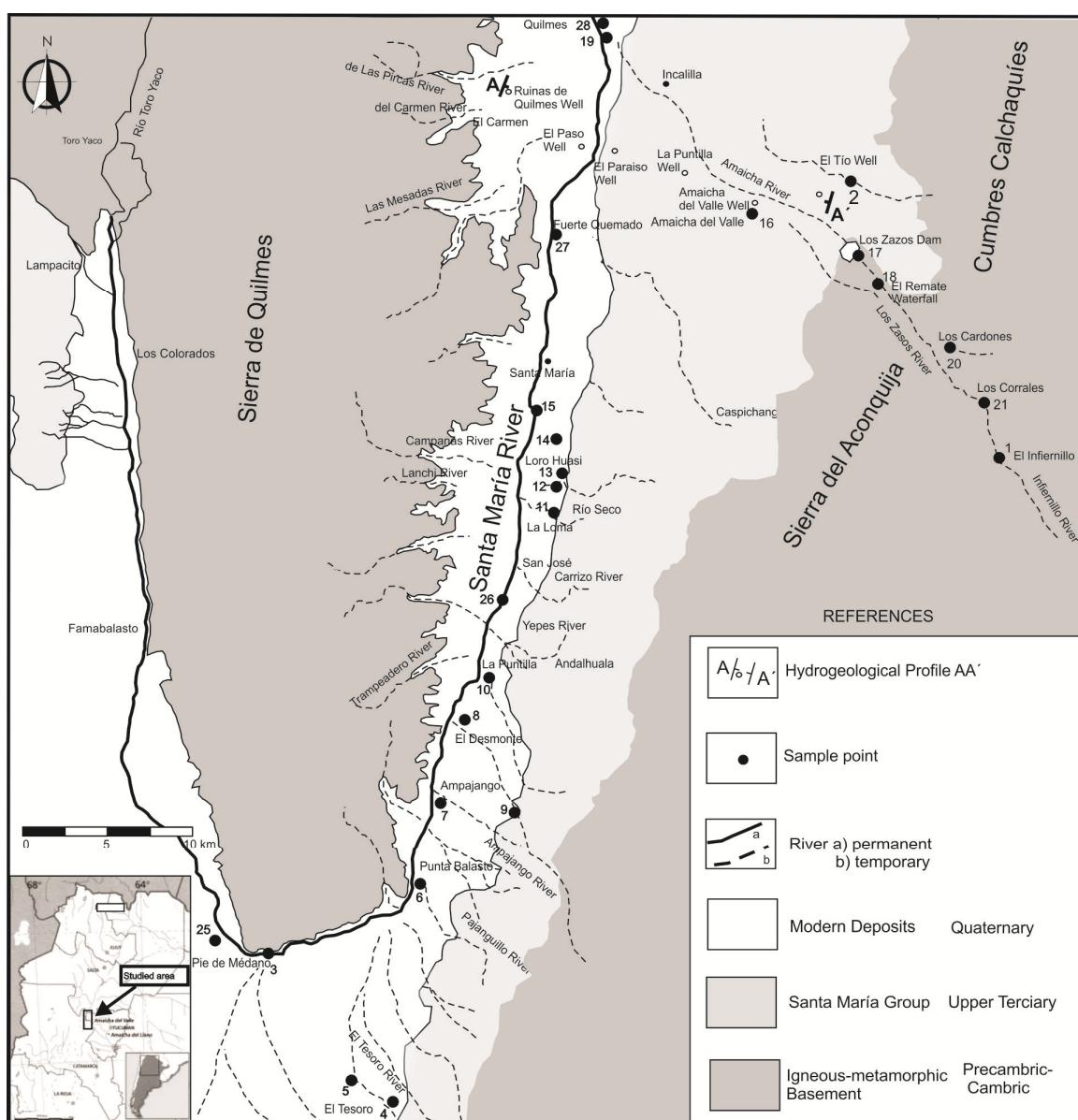


Figure-1: Geological map with the location of the sampling points.

## Methodology

**Study area:** The studied area is part of Santa María Valley, a northwest-southeast tectonic depression from Punta de Balasto in the province of Catamarca, to the north of Cafayate in the province of Salta. The central area of the hydrogeological basin developed in Catamarca territory has a large surface exceeding 1700 Km<sup>2</sup>, draining the water from the high peaks to the valley. The limits of such basin are formed by an igneous-metamorphic basement whose outcrops constitute the cores of the Sierra de Quilmes to the west and Cumbres Calchaquíes-Sierra del Aconquija to the east. The metamorphic basement of the Sierra de Quilmes corresponds to schists and gneisses of low, medium and high grade metamorphism and the Sierra del Aconquija is composed of mica schist, quartz phyllites and banded quartz phyllite. The basement of the central-eastern region consists of metamorphic rocks intruded by several granitic intrusions and scarce basic and ultrabasic rocks with regional anatetic processes. The lithology of Cumbres Calchaquíes basement correspond to a biotiteschists and banded gneisses characterized by the garnet-staurolite association indicating a medium grade metamorphism<sup>15</sup>.

Sedimentites of Santa María Group of Miocene-Pliocene age crop out in the west slope of Sierra de Aconquija - Cumbres Calchaquíes. Santa María Group consists of levels of clay and silt, with interbedded sands with a predominance of yellow and green colors. Outcrops of Tertiary age in terrace levels in the eastern slope of the valley can be observed due to the structure of the region. Reverse faults on the edge of the Sierra de Quilmes allow the development of significant sedimentary deposits in alluvial fans of Quaternary age covering the foothills of Sierra de Quilmes. They are generally coarse sands and gravels with large boulders of metamorphic rocks which form the main reservoirs of groundwater in this area of the valley. Terraced fluvial deposits are observed on the margins of Santa María River. They are selected sands and dunes produced by the effect of strong wind erosion. Coarse fanglomerate of igneous and metamorphic rocks, gravel, coarse sand, silt and conglomerate of metamorphic and volcanic boulders are observed too.

Santa María River is the maximum hydric exponent of the region studied and has a permanent regime with flow peaks during the summer months. It is located in the NW Argentina, at 1900 m above sea level in the intermountain valley of Santa María, 20 -25 Km width between 24° 30' and 26° 30' South Latitude (Figure-1). The river rises from the west side of Sierra de Quilmes as a continuation of Toro Yaco River. Flowing down the valley, the Santa María River receives important tributaries from the west side such as Anchillo, Managua and Pichao Rivers in the northern part of the Sierra de Quilmes outside the area under study as well as other smaller tributaries such as El Carmen, Las Pircas, La Mesada, Campanas and Trampeadero rivers. Santa María River also receives many tributaries from the east that flow down from the peaks of the Sierra del Aconquija: Pajanguillo, Ampajando, Rio Seco, San

José, Loro Huasi, Yasyamayo and Amaicha rivers. At the latitude of Salta Province, the confluence of Santa María, Calchaquí and Las Conchas-Guachipas rivers form Juramento River that downstream merges with the Paraná basin. The annual average flow is 2.8 m<sup>3</sup>.s<sup>-1</sup> and the corresponding spill is 85 Hm<sup>3</sup>.y<sup>-1</sup>. The flow begins to increase in December to reach its highest point in January and February (with six rains by months) and decreases rapidly in April. The annual average precipitation is approximately 200 mm. The climate of the basin is arid as in hills and plains with dry atmosphere and thermal amplitude. Average annual temperature is about 15°C and the maximum and minimum average temperatures are 25°C and 7.0°C, respectively. The heliophany and solar radiation throughout the area are high. The annual average relative humidity is 46%. The average frequency of frost days in Santa María is 65 days in the year<sup>6</sup>.

A hydrogeological cross-section of the Santa María Valley, between Sierra de Quilmes, at west, and Sierra del Aconquija, at east, was observed in Figure-2. Santa María River is the main water collector of the valley and its homonymous basin shows a strong hydric annual deficit, receiving scarce precipitations in the cones of the mountain slopes. A minor input proceeds from surface waters that drain over pre quaternary strata of low permeability through a gentle slope of the glaciis that slides down from the east. The groundwater of the torrents that flow into the valley provides water to the flooded area of Santa María River. Finally, the basin also receives water that infiltrates directly from the main river and other minor water courses of permanent regime. The water courses of the valley are mostly temporary due to the high permeability of the substrate and their intensive use for both human consumption and irrigation. According to the structural features of the valley, both groundwater and surface water flows would have a similar pattern of circulation. The discharge area of the groundwater is located on both sides of the low-flow channel. This region allows the exploitation of groundwater due to the fine granulometry of the subsoil. The water level of this area was located at 14, 21 and 30 m drilling depth at La Soledad, Loro Huasi and Casa de Piedra, respectively. Two confined levels were determined up to 113 m deep (El Puesto drilling). The first one was found at 21 and 57 m deep, with 9, 60 to 35.35 m thick, that increases from Fuerte Quemado to Punta de Balasto. The second confined table is located in Fuerte Quemado and Casa de Piedra, at 36, 50 and 70.30 m deep. Several drillings were carried out in the western side of Santa María River near Fuerte Quemado, with 7 and 20 meters static levels and 200 m<sup>3</sup> water flows per hour. 150 m deep drillings, with 80 m static levels in the left margin up to the alluvial cones and with 25 m in the right margin, were realized in the area of Punta de Balasto.

**Sampling and analyses:** Twenty five water samples were collected in 2014's summer time, seventeen from surface watercourse and eight from groundwater of available wells. Special care was taken not to modify the samples from the moment they are taken until they are analyzed. The location of

the samples were geo-referenced by Garmin GPS eTrex Vista HCx (Figure-1). They were collected in two liters polyethylene containers previously washed with 20% HNO<sub>3</sub> (Merck,p.a.) and rinsed with distilled and deionized water by NANO pure (Barnsted). The samples were filtered through glass fiber filters.

The samples were analyzed in the laboratory and standard methods from American Public Health Association were employed<sup>16</sup>. The parameters determined in water were pH, electrical conductivity (EC), major ions (calcium, magnesium, sodium, potassium, chloride, sulphate, carbonate and bicarbonate) and Total Dissolved Solids (TDS). The determinations were made within 48 h after collection except for bicarbonate that was analyzed within 24 h. The pH was measured by direct potentiometry with a Mettlerp Hmeter Delta 320 and a combined glass electrode. The EC was measured by direct conductimetry with Tacussel conductimeter CD 78. The TDS values were obtained from conductivity data. Calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>) were determined by

complexometric titration with EDTA standardized solution. The concentration of sodium (Na<sup>+</sup>) and potassium (K<sup>+</sup>) were measured by flame photometry. Chloride (Cl<sup>-</sup>) was determined by standard AgNO<sub>3</sub> titration. The sulphate (SO<sub>4</sub><sup>2-</sup>) determination was realized by turbidimetry. Carbonate (CO<sub>3</sub><sup>2-</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>) were determined by titration with HCl standardized solution. The analytical precision of ions was determined by calculating the ionic balance error which was within 5%. The quality of the analyses is provided by the successful annual participation of the laboratory in the international inter-laboratory exercises for major, minor and trace constituents conducted by the National Institute of Industrial Technology of Argentina (INTI) on certified water. The results obtained from the physicochemical analysis carried out in the water samples, as well as in the site of sampling and its geographical coordinates, are shown in Tables-1 and 2. In all cases the results are expressed by the number of significant figures according to the analytical technique used for its determination.

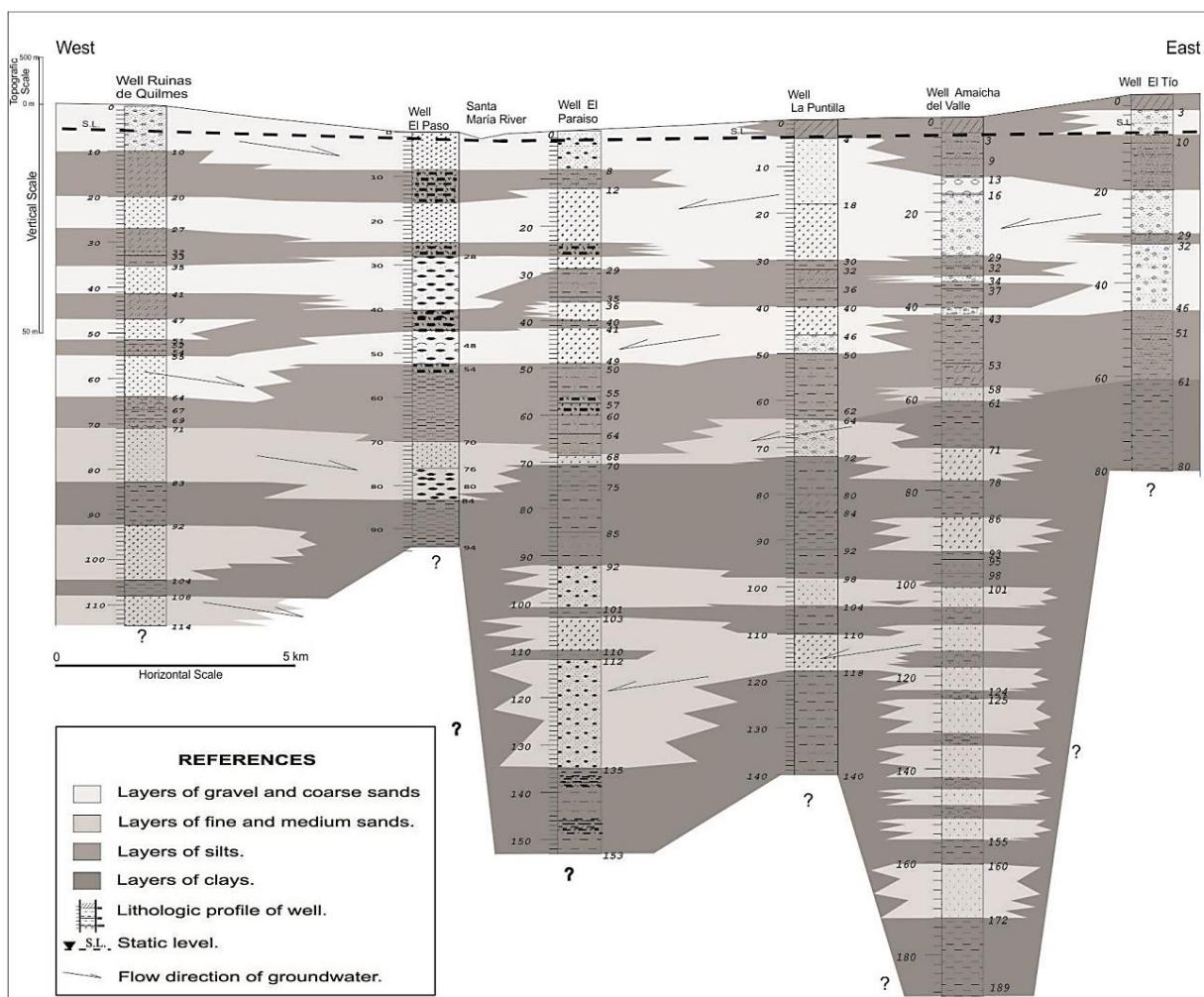


Figure-2: Hydrogeological cross-section of Santa María Valley.

**Table-1:** Water samples: location, characteristics, pH, EC, TDS.

ID Sample	Site/Characteristics	Latitude	Longitude	pH	EC ( $\mu\text{S cm}^{-1}$ )	TDS ( $\text{mg L}^{-1}$ )
M6	Punta de Balasto place/ well	26°57'48.30"S	66° 8'37.00"O	8.09	300	192
M7	Punta de Balasto place/well	26°55'30.00"S	66° 7'0.10"O	7.94	347	222
M8	El Desmonte place/well	26°52'49.10"S	66° 6'3.80"O	7.91	316	202
M11	La Loma place/cistern	26°45'41.70"S	66° 3'22.70"O	8.09	386	247
M12	Loro Huasi place/well at south	26°45'8.20"S	66° 3'15.35"O	7.94	673	431
M13	Loro Huasi place/well at center	26°44'47.50"S	66° 3'12.40"O	8.11	355	227
M14	Santa María place/well	26°43'25.78"S	66° 3'16.70"O	7.94	850	544
M16	Amaicha del Valle place/well	26°35'36.50"S	65°55'10.70"O	7.88	1482	948
M1	Infiernillo river	26°44'0.30" S	65°47'12.30"O	7.40	100	64
M2	El Tío/spring water	26°34'50.60"S	65°52'23.90"O	7.85	963	616
M3	Santa María river	27° 0'0.80"S	66°13'59.20"O	8.15	411	263
M4	El Tesoro river	27° 4'41.20"S	66° 9'14.60"O	8.26	270	173
M5	El Tesoro dam	27° 4'3.30"S	66°10'53.70"O	8.09	273	174
M9	Ampajango river	26°55'36.70"S	66° 4'46.30"O	8.03	214	137
M10	La Puntilla/waterway	26°51'8.40"S	66° 5'48.90"O	8.09	230	147
M15	Santa María river (at Santa María)	26°42'29.10"S	66° 3'42.30"O	8.45	743	476
M17	Amaicha river (at Los Zazos)/dam	26°37'34.60"S	65°52'15.40"O	8.25	302	193
M18	Amaicha river (at El Remate)/waterfall	26°38'21.40"S	65°51'30.80"O	7.45	375	240
M19	Santa María river (at Quilmes bridge)	26°30'31.80"S	66° 0'33.90"O	8.56	2711	1735
M20	Los Cardonesriver	26°40'17.80"S	65°49'3.80"O	8.30	251	161
M21	Infiernillo river (Los Corrales)	26°42'16.40"S	65°48'1.00"O	7.92	149	95
M25	Santa María river (Punta Balasto)	26°59'26.54"S	66°15'43.59"O	8.40	302	193
M26	Santa María river (San José)	26°48'50.04"S	66° 5'2.44"O	8.30	280	179
M27	Santa María river (Fuerte Quemado)	26°37'5.63"S	66° 2'43.01"O	8.50	3480	2227
M28	Santa María river (Quilmes)	26°30'0.25"S	66° 0'32.49"O	8.30	2423	1550

**Table-2:** Water samples: major chemical composition.

ID Sample	Cl <sup>-</sup> (mg L <sup>-1</sup> )	HCO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	CO <sub>3</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	Na <sup>+</sup> (mg L <sup>-1</sup> )	K <sup>+</sup> (mg L <sup>-1</sup> )	Ca <sup>2+</sup> (mg L <sup>-1</sup> )	Mg <sup>2+</sup> (mg L <sup>-1</sup> )
M6	17.52	147.8	ND	12.0	29.1	18.6	22.61	5.710
M7	17.52	151.6	ND	22.8	25.9	15.7	29.22	10.14
M8	9.470	163.0	ND	12.6	14.0	14.8	33.74	10.78
M11	9.270	125.1	ND	21.6	9.60	9.20	22.96	10.56
M12	40.49	263.4	ND	63.5	72.5	19.0	51.83	11.09
M13	15.61	181.9	ND	10.9	33.0	15.9	27.83	8.240
M14	65.66	295.6	ND	85.8	86.0	18.0	65.05	13.31
M16	106.0	337.3	ND	288	138	34.2	133.0	24.83
M1	6.340	58.75	ND	3.02	6.80	7.30	9.560	3.430
M2	89.84	178.1	ND	146	92.5	24.8	76.52	19.02
M3	30.62	148.8	ND	44.9	32.0	17.7	36.00	9.830
M4	11.28	141.2	ND	7.69	16.4	11.7	25.74	9.300
M5	9.060	152.6	ND	8.26	16.0	11.3	28.87	8.880
M9	8.260	130.8	ND	5.70	8.30	7.50	20.52	9.930
M10	26.79	147.8	ND	37.6	30.5	12.7	34.44	8.450
M15	53.18	274.8	67.11	34.2	71.0	25.5	63.31	10.56
M17	15.51	119.4	24.23	17.5	24.0	15.9	26.09	6.760
M18	18.53	117.5	ND	22.4	30.0	17.9	27.83	8.660
M19	366.6	490.8	59.65	316	470	45.4	65.05	13.10
M20	10.98	134.6	5.590	5.54	17.4	15.9	22.61	7.400
M21	7.860	79.60	ND	6.72	10.0	9.80	14.61	4.970
M25	15.00	100.6	ND	16.7	20.1	2.90	28.90	5.700
M26	17.00	103.7	ND	16.3	18.7	4.60	25.90	6.900
M27	513.0	745.7	42.00	283	600	24.8	147.9	5.200
M28	303.0	571.8	12.00	145	410	17.7	74.80	3.900

## Results and discussion

**Water chemistry:** Table-1 shows the pH, EC and TDS values for groundwater and surface waters. The maximum pH is 8.56

and the minimum is 7.40, indicating that the pH of water samples is well within the natural water limits. The electrical conductivity (EC) values ranged from 300 to 1482  $\mu\text{S.cm}^{-1}$  for groundwater samples while for surface waters they lie between

100 and 3480  $\mu\text{S.cm}^{-1}$ . TDS ranges from 64 to 2227  $\text{mg.L}^{-1}$  for all the samples.

Table-2 provides information about major chemical composition for surface and ground water. For ground water, among cations, the concentration of  $\text{Na}^+$  ions (in  $\text{mg.L}^{-1}$ ) ranged from 9.6 to 138,  $\text{K}^+$  from 9.20 to 34.2,  $\text{Ca}^{2+}$  from 22.61 to 133.0, and  $\text{Mg}^{2+}$  from 5.710 to 24.83. Sodium and calcium have similar abundances, about 38% average (in  $\text{meq.L}^{-1}$ ), whereas magnesium represents 16% and potassium only 7.7%. In the case of the anions, the concentrations of  $\text{Cl}^-$  (in  $\text{mg.L}^{-1}$ ) varies between 9.270 and 106.0,  $\text{SO}_4^{2-}$  between 10.9 and 288 and  $\text{HCO}_3^-$  between 125.1 and 337.3. Bicarbonate is dominant and it represents an average of 57% of the total anions. Then, the order of abundances of anions of secondary importance is sulphate (22%) > chloride (16%). Carbonate was not detected.

For surface water samples, among cations the concentration of  $\text{Na}^+$  ions (in  $\text{mg.L}^{-1}$ ) ranged from 6.80 to 600,  $\text{K}^+$  from 2.90 to 45.4,  $\text{Ca}^{2+}$  from 9.560 to 147.9, and  $\text{Mg}^{2+}$  from 3.430 to 19.02. The order of abundance is  $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$  representing an average of 58%, 28%, 9% and 5% of the total cations. Among the anions, the concentration of  $\text{Cl}^-$  (in  $\text{mg.L}^{-1}$ ) varies between 6.340 and 513.0,  $\text{SO}_4^{2-}$  between 3.02 and 316 and  $\text{HCO}_3^-$  between 58.75 and 745.7. Bicarbonate is dominant

representing an average of 48% of the total anions. Then, the order of abundances of anions of secondary importance is chloride (32%) > sulphate (18%). Carbonate was detected only in six samples out of twenty with values between 5.6 and 67.0  $\text{mg.L}^{-1}$ . Bicarbonate is the predominant anion while calcium and sodium are the predominant cations in all water samples.

The quality of these chemical characteristics was evaluated by comparing them with the maximum permissible limits for potable water given by WHO<sup>17</sup>. Most of the samples have EC and TDS within the limit of 1480  $\mu\text{S.cm}^{-1}$  and 1000  $\text{mg.L}^{-1}$  (Table-1) respectively. Santa María River exceeds the established limit at the northern of the area (Fuerte Quemado and Quilmes). The WHO guiding limit for  $\text{SO}_4^{2-}$  is 400  $\text{mg.L}^{-1}$ . All the samples are within the maximum permissible limit.  $\text{Cl}^-$  contents are well within the maximum limit of 500  $\text{mg.L}^{-1}$ , except one surface sample at the north (Quilmes).

The contents of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  in the Santa María River only exceed the permissible limits at the same locations with EC elevated (Fuerte Quemado and Quilmes).

**Hydrochemical facies:** Water classification was studied using the Piper diagram in order to identify the processes that control the water chemistry (Figure-3).

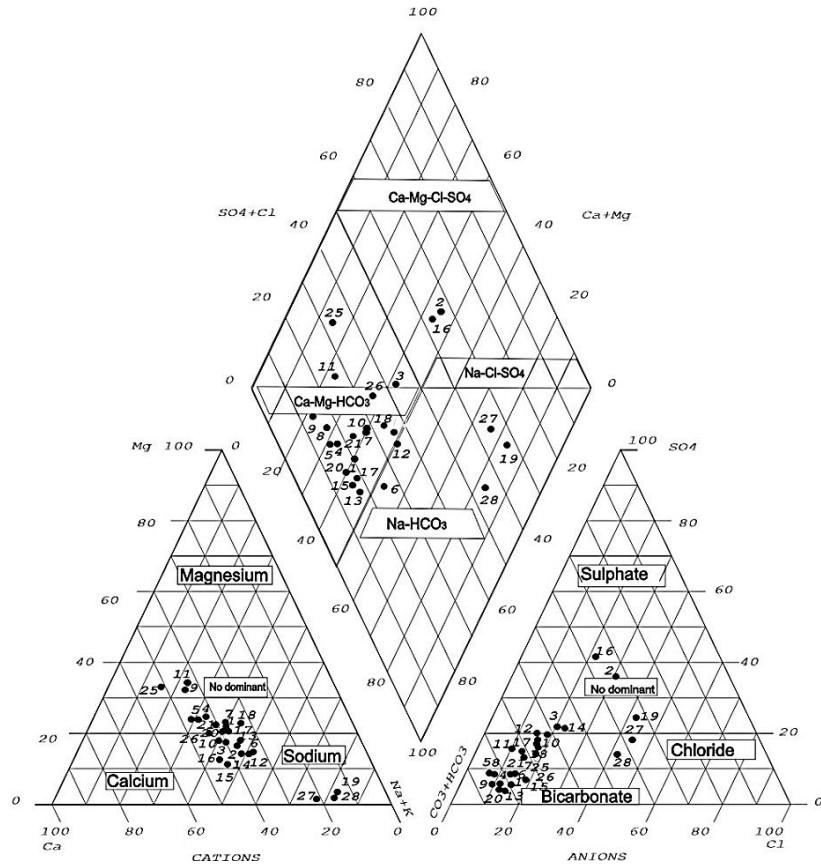


Figure-3: Piperdiagram.

**Ca-Na-HCO<sub>3</sub>:** 4-El Tesoro river, 5-El Tesoro (dam), 8-El Desmonte (well), 10-La Puntilla (water way), 20-Los Cardones river, 21-Infiernillo river, 26- Santa María river (San José), 1-Infiernillo river, 3-Santa María river (Pie de Médano), 7- Punta de Balasto (well), 13- Loro Huasi (well), 14- Santa María (well), 15- Santa María river (Sta. María), 17- Los Zazos river, 18- Amaicha river (El Remate waterfall).

**Na-HCO<sub>3</sub>:** 6-Punta de Balasto (well), 12-Loro Huasi (well of south).

**Ca-HCO<sub>3</sub>:** 25-Santa María River (Punta Balasto).

**Ca-Mg-HCO<sub>3</sub>:** 9-Ampajango river, 11- La Loma (San José, cistern).

**Na-Cl-HCO<sub>3</sub>:** 19-Santa María river (Quilmes bridge), 26- Santa María river (San José), 27-Santa María river (Fuerte Quemado).

**Ca-Na-SO<sub>4</sub>-HCO<sub>3</sub>:** 16- Amaicha del Valle (well), 2- El Tío (spring water).

The following groups were identified. The Ca-Na-HCO<sub>3</sub> water type is predominant in Santa María valley with different proportion of sodium and calcium, which represent 60% of the total number of water samples analyzed. Na-HCO<sub>3</sub> water types were found in Punta Balasto and Loro Huasiground waters. In the southern part of the valley, Santa María River presents Ca-HCO<sub>3</sub> watertype whereas the Ampajango River and La Loma groundwaters contain Mg-Ca-HCO<sub>3</sub> type of water.

High chloride concentrations were observed (Na-HCO<sub>3</sub>-Cl water type) in Santa María River in the north of the area between Fuerte Quemado and Quilmes towns. This would indicate a higher evolution and/or significant contributions of saline water drained by tertiary materials of Santa María Group that outcrop on the east bank of Santa María River on the slope of Sierra del Aconquija. In addition, some considerations should be given to the high uptake of surface water for human and agricultural use in the town of Santa María and its surrounding areas.

An increase of sulphate ion (Ca-Na-HCO<sub>3</sub>-SO<sub>4</sub> water type) is observed in Amaicha del Valle zone due probably to the flow of water from a substrate rich in gypsum banks, described for tertiary sediments of the area.

The origin of this type of waters in the basin may be due to the interaction between groundwater and surface waters withvarious rocks with several mineralogical compositions distributed in the region.

In general, a significant increase in the degree of water mineralization of Santa María River in the direction south-north is observed. The other rivers present least mineralized waters except, at the northeast of the region, sulphate contribution is observed in surface waters. All ground waters have low mineralization.

**The origin of solutes:** From the graphs representing the concentration ratios of the dissolved ions in the waters the processes that gave rise to the observed composition can be

determined. The Na-Cl relationship has often been used to identify the mechanism for acquiring salinity<sup>18</sup>. Figure-4 shows the correlation diagram between Na and Cl for surface and groundwater samples. Both cases showa very high positive correlation with 0.9971 and 0.9857 values, respectively, indicating that Cl<sup>-</sup> and Na<sup>+</sup> were derived from halite dissolution. A Na/Cl molar ratio greater than one that indicates excess of Na<sup>+</sup> relative to Cl<sup>-</sup><sup>19</sup> was observed (Figure-4). Thus, a probable source of Na in weathering of albite to kaolinite that releases Na<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> may exist. Figure-4 also shows a strong correlation between Na<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> for surface ( $r=0.9754$ ) and groundwater ( $r=0.9692$ ).

**Calcite dissolution:** The calcite is dissolved giving a  $\frac{1}{2}$  Ca<sup>2+</sup>:HCO<sub>3</sub><sup>-</sup> equivalence ratio 1:1. Figure-5 shows the relationship between Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> with HCO<sub>3</sub><sup>-</sup> for surface and groundwater. A positive correlation coefficient between Ca and HCO<sub>3</sub><sup>-</sup> suggests the dissolution of calcite that incorporates Ca<sup>2+</sup> to the water (0.8997 and 0.8954, respectively). There is no relationship between Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> for surface waters because the correlation coefficient is not significant ( $r=0.0057$ ). This indicates that the source of Mg<sup>2+</sup> could be another mineral like biotite and chlorite present in the basement of the area. Ground water has a  $r=0.7849$  for this relation which indicates at least partial dissolution of dolomitic rocks. Figure-5 also shows a good correlation between K<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> ( $r=0.6252$  for surface and  $r=0.7973$  for ground waters) that would be expected for the K-feldspar dissolution<sup>20</sup>.

**Gypsum dissolution:** Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> in surface and groundwater showed a good relationship (Figure-6) which suggests that a simple gypsum dissolution could exert a control on calcium chemistry ( $r=0.8294$  and 0.9880, respectively). There is a strong correlation between Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> and Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> in groundwater indicating dissolution of sodium and magnesium minerals present in deeper layers, whereas only the Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> correlation is good in surface waters ( $r=.9342$ ).

A charge balance between Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> indicates that surface and groundwater samples were derived from simple dissolution of calcite, dolomite and gypsum ( $r=0.8749$  and 0.9977) (Figure-7).

**Cation exchange:** The bivariate plot of (Ca<sup>2+</sup> + Mg<sup>2+</sup> - SO<sub>4</sub><sup>2-</sup> - HCO<sub>3</sub><sup>-</sup>) vs. (Na<sup>+</sup> + K<sup>+</sup> - Cl<sup>-</sup>) shows the Na<sup>+</sup> exchange for Ca<sup>2+</sup> and Mg<sup>2+</sup>.

Those samples in which the cation exchange was an important composition-controlling process, the relationship between these two parameters would be linear with a slope of -1. Figure-7 indicates an increase in Na<sup>+</sup> related to a decrease in (Ca<sup>2+</sup> + Mg<sup>2+</sup>) or an increase in (HCO<sub>3</sub><sup>-</sup> + SO<sub>4</sub><sup>2-</sup>). The array of surface and groundwater data plots close to the straight line with a slope near -1, indicating that essentially all Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> participated in the ion exchange reaction.

Natural waters present low levels of  $K^+$  as a consequence of their tendency to be fixed by clay minerals and to participate in secondary minerals<sup>21</sup>. A good correlation between  $K^+$  and  $Cl^-$  ( $r= 0.6647$  for surface water and  $r=0.8856$  for groundwater) indicates that the weathering of sylvite ( $KCl$ ) partially controls the  $K^+$  chemistry (Figure-7).

A conceptual model of the studied areas suggested, determining the recharged areas and sense of groundwater runoff. The recharge is given by torrential rains that occur in summer in the region, although there is a high water deficit. There are also spring waters in elevated sectors of the basin providing water most of the year to the ravines developed on basement rocks. This water flow is supplied to the Santa Maria River, which runs in this zone from south to north.

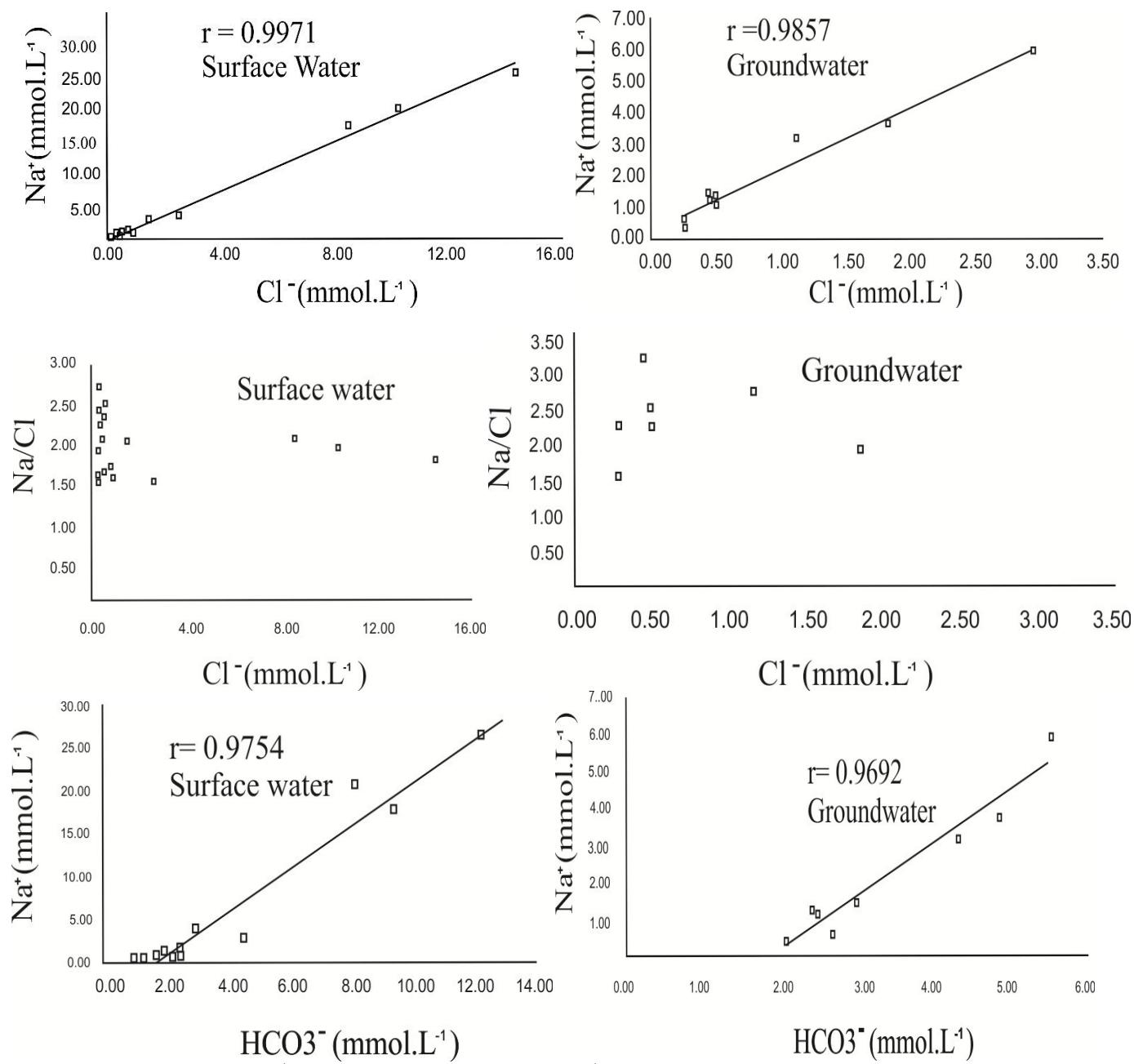
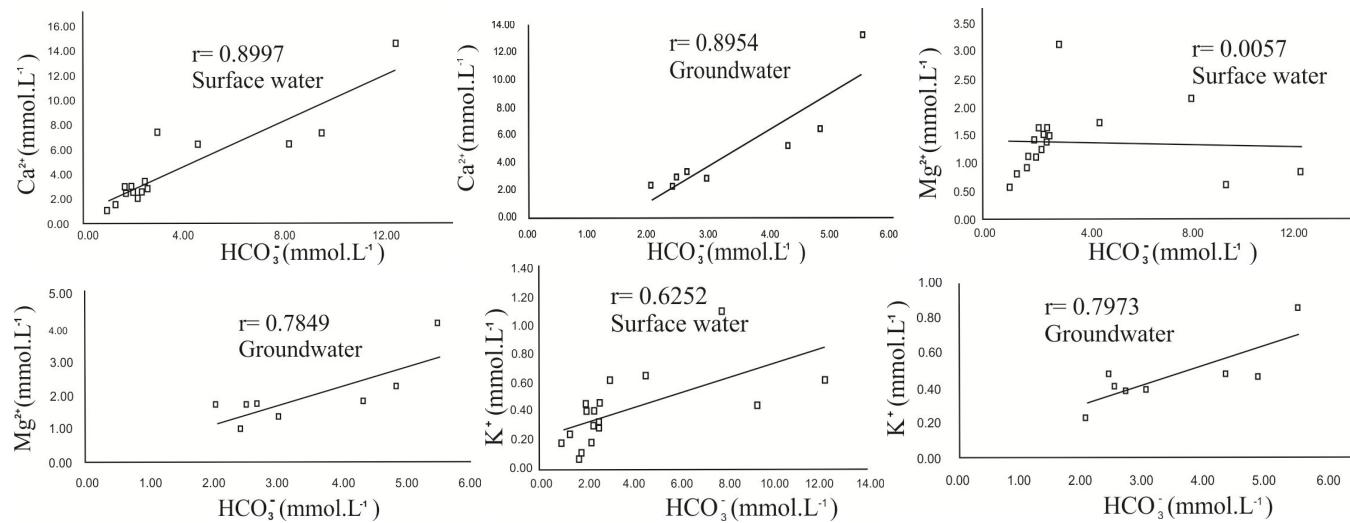
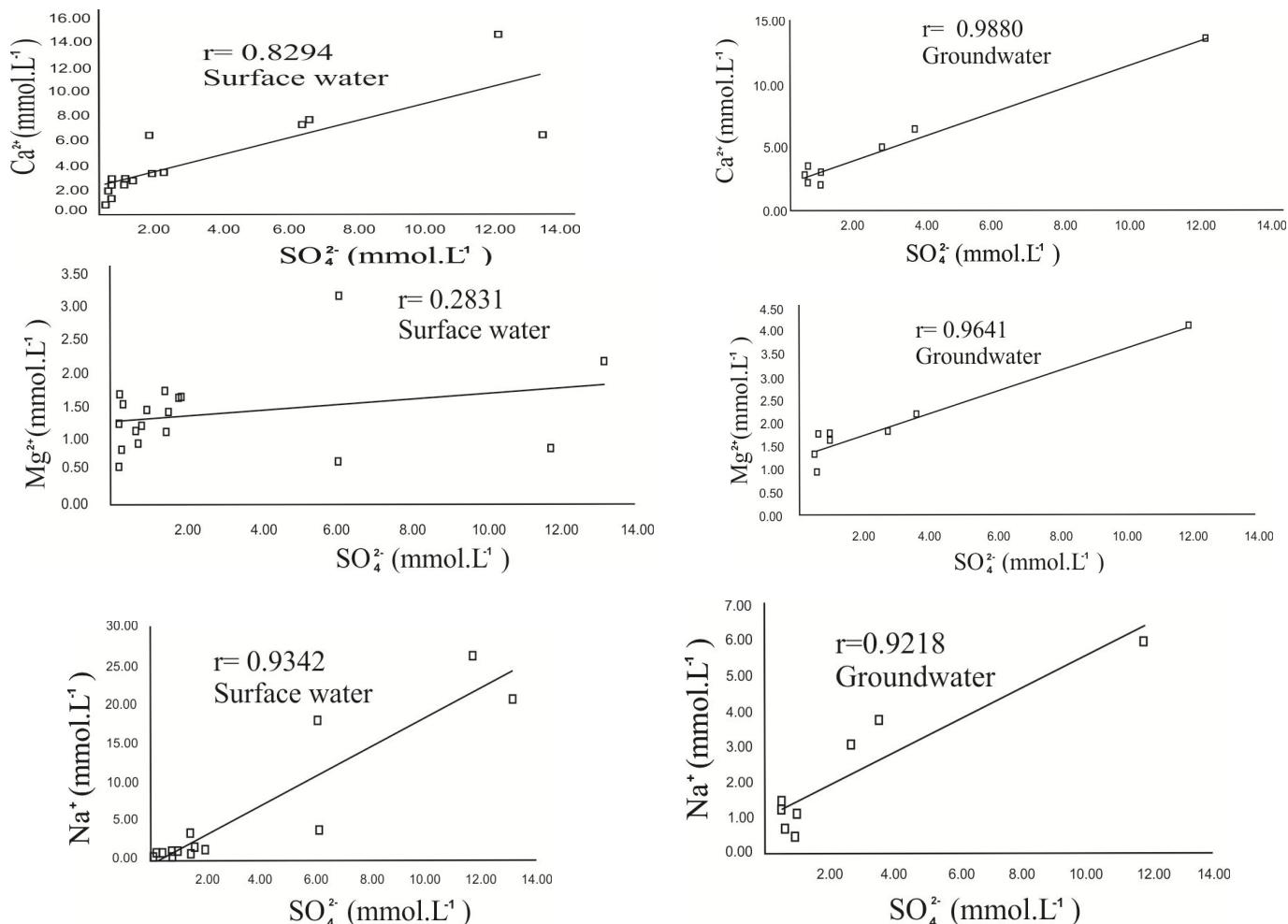


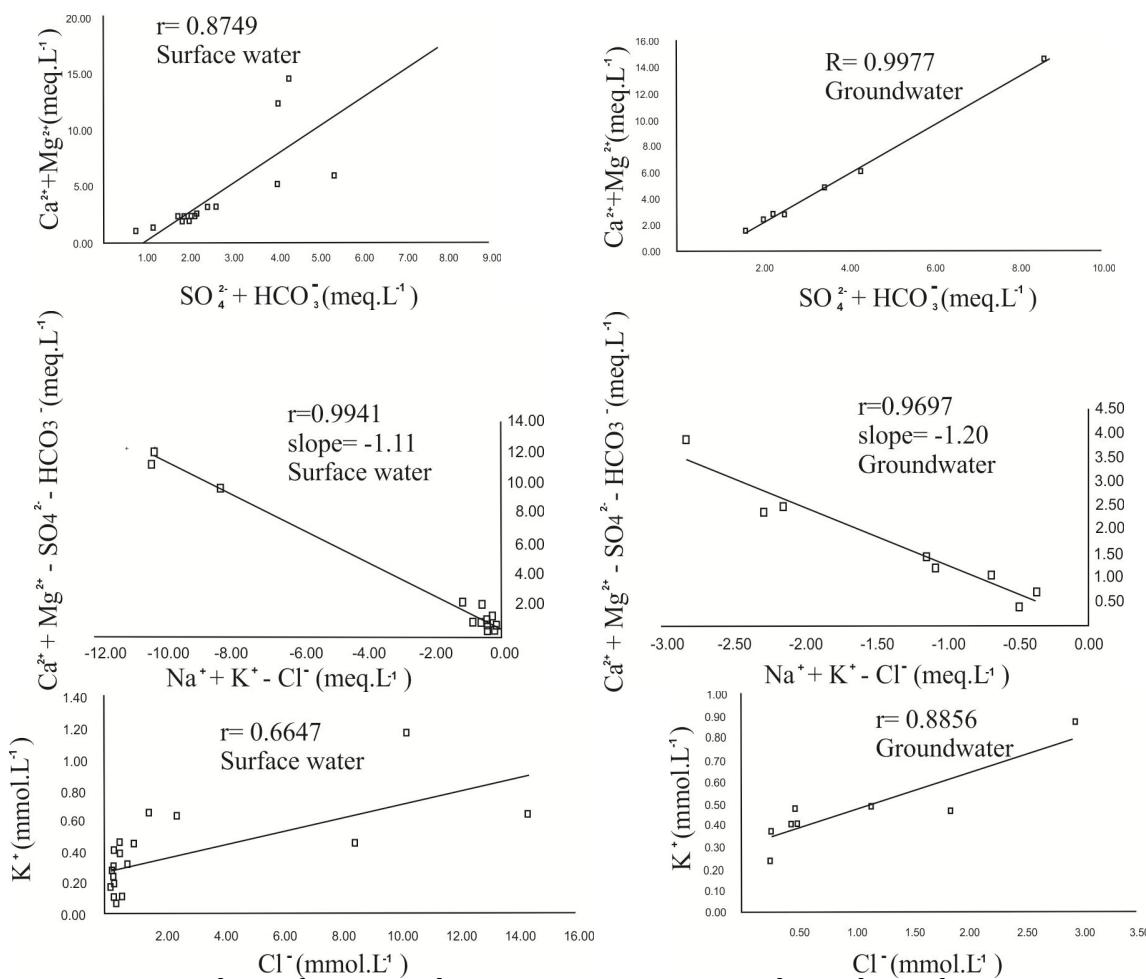
Figure-4:  $Na^+$  versus  $Cl^-$ ,  $Na/Cl$  ionic ratio and  $Na^+$  versus  $HCO_3^-$  for surface and groundwaters.



**Figure-5:**  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  versus  $\text{HCO}_3^-$  concentrations for surface and groundwaters.



**Figure-6:**  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  versus  $\text{SO}_4^{2-}$  concentrations for surface waters and groundwaters.



**Figure-7:** Relation between  $\text{Ca}^{2+} + \text{Mg}^{2+}$  versus  $\text{SO}_4^{2-} + \text{HCO}_3^-$ , relation between  $\text{Ca}^{2+} + \text{Mg}^{2+} - \text{SO}_4^{2-} - \text{HCO}_3^-$  versus  $\text{Na}^+ + \text{K}^+ - \text{Cl}^-$  and relation between  $\text{K}^+$  and  $\text{Cl}^-$  for groundwater and surface water.

## Conclusion

The hydrochemical characteristics in the Santa María Valley vary in relation to different water-rock interactions that occur. There are rocks with several mineralogical compositions distributed in the area. There is a predominance of Ca-Na-HCO<sub>3</sub> water type in Santa María Valley. Ca-Na-HCO<sub>3</sub>-SO<sub>4</sub> water type is found in Amaicha del Valle, northeast of the area under study. This is associated with the presence of gypsum banks interleaved with sedimentary rocks of Santa María Group. In general, a significant increase in the degree of water mineralization was observed in the downstream area of Santa María River. The great water uptake for human and farming use in the north of Santa María River is associated with the Na-HCO<sub>3</sub>-Cl water type, apart from the presence of salts from the substrate. Dissolution of calcite will add significant amounts of Ca<sup>2+</sup> to surface and groundwater. Dissolution of dolomitic rocks gives Mg<sup>2+</sup> to the ground water while aluminosilicate minerals present in the basement of the area could be the source of Mg<sup>2+</sup> in the surface water. The contents of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup> and Ca<sup>2+</sup> in surface and groundwater are determined by the dissolution of

halite and gypsum. The content of Na<sup>+</sup> may be due to cation exchange of Na<sup>+</sup> for Ca<sup>2+</sup> and Mg<sup>2+</sup> and the weathering of minerals like biotite and chlorite. The contribution of K<sup>+</sup> to the water of the area is modest because of its tendency to be fixed by clay minerals and to participate in the formation of secondary minerals. The K<sup>+</sup> content derives mostly from K-feldspar dissolution.

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