



# Geochemical mechanisms controlling the chemical composition of groundwater and surface water in the southwest of the Pampean plain (Argentina)



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## ABSTRACT

The Pampean plain is one of the most extended regions of the world. In this plain there are numerous shallow lakes that have different origins associated with climate changes at the end of the Quaternary period. Chasicó Lake is the main waterbody in the southwest of the Chaco-Pampean plain. It shows some differences from the typical Pampean shallow lakes. The aim of this paper is to explain the geochemical process that determines the chemical composition of the water of Chasicó Lake. The results show that the groundwater is sodium bicarbonate type. Chebotarev's diagram indicates that the cation-exchange takes place in groundwater. The surface water of Chasicó Lake is sodium chloride type. Gibbs's diagram shows that the geochemical processes that affects the Chasicó Lake are evaporation and crystallization, being the water of the lake similar to seawater. The BEI (Base Exchange Index) shows that the process of cation-exchange in the water is not relevant. As, F and V concentrations were studied in surface and groundwater showing significant correlations in groundwater between As vs. F ( $r = 0.99, p < 0.05$ ), As vs. V ( $r = 0.99, p < 0.05$ ) and V vs. F ( $r = 0.99, p < 0.05$ ), while in surface water it was only found for As vs. F ( $r = 0.91, p < 0.05$ ). The As, F and V concentration values were higher and more widely dispersed in surface water than in groundwater, as a consequence of evaporation. The fact that these elements do not correlate in surface water may also indicate a different origin.

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## 1. Introduction

The Chaco-Pampean plain is one of the most extended regions of the world. The development of wetland systems and very shallow lakes (Iriondo and Drago, 2004) have a straight relationship with the climate and geomorphology of the region, which play a significant role in the overall hydrological cycle of the Buenos Aires province (Argentinean Southern Pampa).

Pampean shallow lakes have various origins associated with climate changes at the end of the Quaternary period, but without lakes as predecessors, including deflation by eolian action and tectonic action, or abandoned fluvial beds, isolated lagoons, and old estuaries (Iriondo et al., 2009). These shallow lakes show typical profile of “*pfanne*” or “*wanne*” (Miretzky et al., 2001). These shallow lakes are alkaline ecosystems, with circulation patterns characteristic of polymictic lakes (average depth of 1.5 m). This implies nearly continuous vertical mixing promoting high concentration of suspended particulate matter and low transparency. The water column is almost always thermally

homogeneous and saturated with dissolved oxygen, and is characterized by a high content of dissolved organic matter, mainly humic substances (Conzonno and Fernandez Cirelli, 1987, 1988). The Pampean sediment, known as Pampean loess, has volcanic pyroclastic origin. Based on the description of Teruggi (1957), the sand fraction of the Pampean loess is formed by plagioclases, alkaline feldspar, intermediate feldspar (andesine), as well as by volcanic lithoclasts, quartz, and volcanic glass. The composition of the silt fraction is similar to the sand fraction, but contains a great amount of fresh and altered volcanic glass shards. Montmorillonite is the clay mineral in this region. Calcium carbonate is also found in the Pampean loess as calcite (8%). Cation exchange capacity of loessic sediments plays an important role in determining the chemical evolution of groundwater (Miretzky et al., 2000), which is strongly associated with Pampean shallow lakes, as reported by Fernández Cirelli and Miretzky (2004).

The Chasicó Lake is the main water body in the southwest of the Chaco-Pampean plain. It shows some differences from the typical Pampean shallow lakes, namely, its tectonic and eolic origin, greater depth, and high salinity (Volpedo and Fernández Cirelli, 2013).

The elevated concentrations of As and F in surface waterbodies (Puntoriero et al., 2014; Rosso et al., 2011a, 2011b) and in groundwater (Alarcón-Herrera et al., 2013; Nicolli et al., 2012) that were reported in the region, suggest that there may be a relationship between surface water and groundwater. However, in these regions the geochemical

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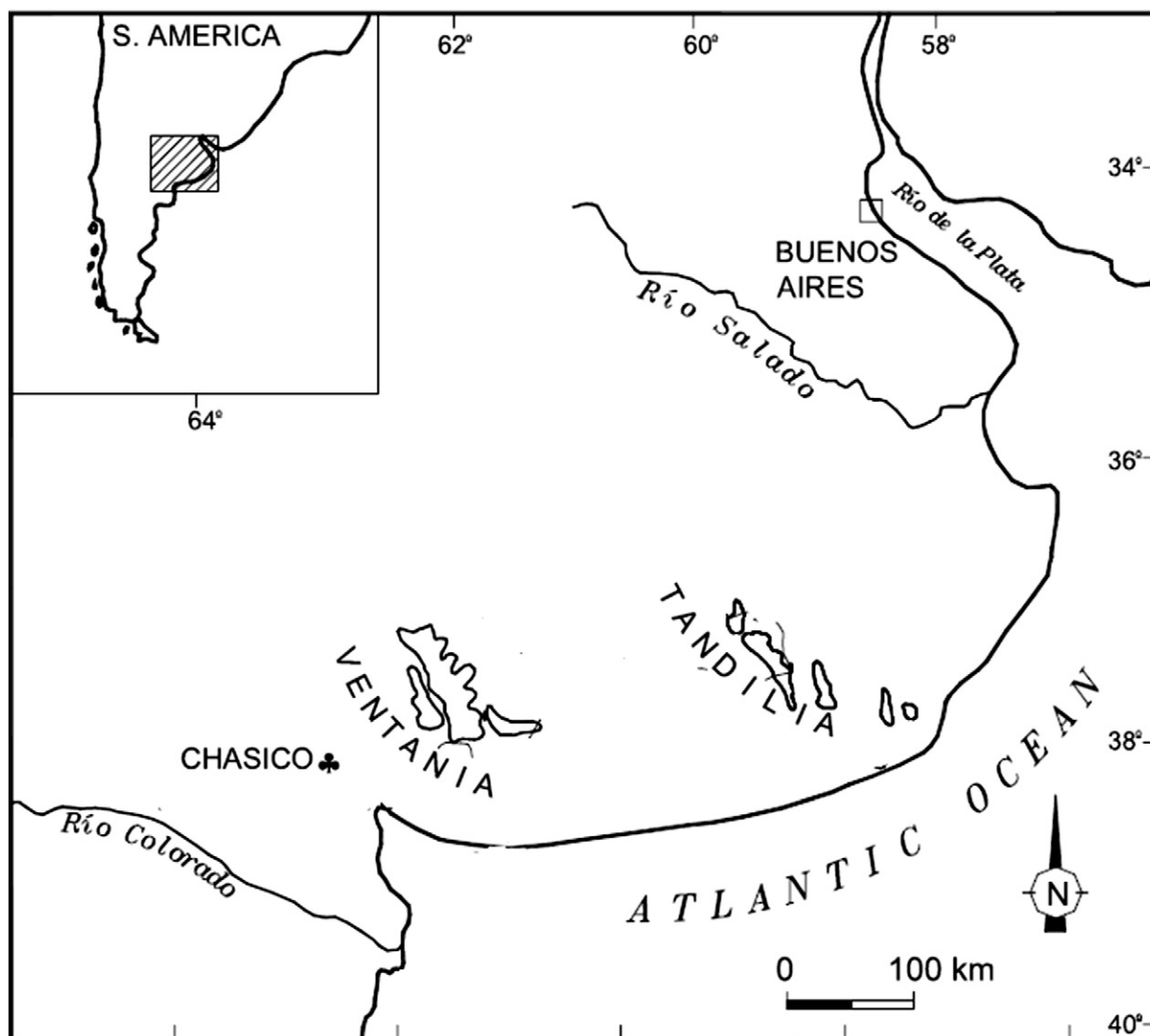


Fig. 1. Chasicó Lake location.

processes that explain the chemical composition of Chasicó Lake were not studied.

The geochemical processes that may explain the composition of surface water in Chasicó Lake are analyzed and discussed in this paper and compared with those occurring in the typical pampasic shallow lakes (pampasic ponds).

## 2. Study area

The Chasicó Lake is an endorheic system that receives the waters of the Chasicó Stream and drains into the Ventania system (Fig. 1). It is placed on a tectonic belt located more than 20 m below sea level, on southwest slopes of the orographic Ventania system. This strip extends in a northwest to southeast direction, parallel to the tectonic pit inside which is located the Colorado River. The late Tertiary succession of the southern Pampean region comprises an extensive plateau capped by a thick calcrete crust, which in turn is covered by a thin apron of late Pleistocene–Holocene eolian deposits (Zárate et al., 2007). Geologically, in the Quaternary period, the sea ingression and regression left ancient salts.

The lake recharge occurs from direct precipitation, groundwater system and surface runoff from a reception basin of 3764 km<sup>2</sup> (Bonorino et al., 1989).

The area of the Chasicó Lake was of 31 km<sup>2</sup> in 1963, increased to 85 km<sup>2</sup> in 2003–2004, and decreased to 50.3 km<sup>2</sup> at present (Remes and Colautti, 2003). This may be the result of natural periods of flooding and drought, which were reflected in salinity and aquatic biota changes. The average maximum depth of this water body is 16 m.

## 3. Sampling and analytical methods

### 3.1. Sampling

Water was sampled in March (wet period) and August (dry period) during 2010 and 2011 (Fig. 2). The values of precipitations and temperature in both periods were: wet period 2010: precipitations: 120.8 mm, temperature: 26.6 °C and 2011: precipitations: 109.3 mm, temperature: 27.3 °C; dry period 2010: precipitations: 3.9 mm, temperature: 16.3 °C and 2011: precipitations: 3.7 mm; temperature: 15.9 °C (Servicio Meteorológico Nacional, 1992). The samples were taken from the surface of the pelagic zone of the Chasicó Lake and from the Chasicó Stream ( $N = 10$ ). Groundwater samples ( $N = 10$ ) were collected from wells (average depth of 7–15 m, depending on the specific construction characteristics) used for human consumption in the Chasicó locality, and from the forest center “Alexander Humboldt” (depth of 650 m) (S 38°38.826 W 63°01.114) (Fig. 2). Groundwater of the latter is of geothermal origin. Samples were taken in triplicate, filtered through a

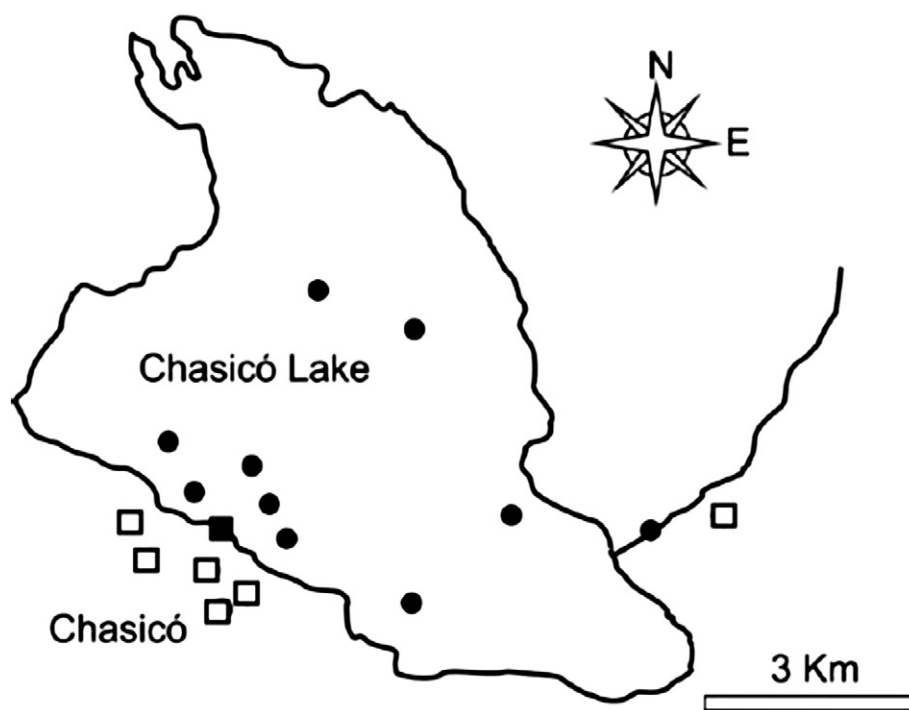


Fig. 2. Samples sites in surface water (white squares) and groundwater (black circles) in Chasicó Village.

0.45- $\mu\text{m}$  acetate cellulose membrane (Micro Separations Inc., MSI), and stored in polyethylene bottles.

### 3.2. Analytical methods

Water temperature and pH were measured *in situ* by a portable pH meter (Hanna HI 9025). All samples were georeferenced using a Garmin GPS. Major ions were determined by standard methods (APHA, 1993): acid titration for carbonates and bicarbonates,  $\text{AgNO}_3$  titration for chloride, precipitation titration with  $\text{BaCl}_2$  for sulfate; atomic emission spectrophotometry for  $\text{Na}^+$  and  $\text{K}^+$ ; and EDTA titration for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . All measurements were made in triplicate (standard deviation less than 4%). Total dissolved solids (TDS) were calculated as the sum of ionic concentrations. Fluoride (F) was determined by the electrometric method of fluoride selective electrode, and the arsenic (As) and vanadium (V) concentrations by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), using a Perkin Elmer Optima 2000 DV optical emission spectrometer. The ICP-AES detection limits were of  $10 \mu\text{g L}^{-1}$  for As and  $8 \mu\text{g L}^{-1}$  for V.

Table 1

Physico-chemical parameters (mean values  $\pm$  standard deviation) of groundwater from the Chasicó locality and forest center Alexander Von Humbolt, during wet and dry periods.

	Chasicó Village		A. Von Humbolt
	Wet period	Dry period	Wet period Dry period
pH	7.73 $\pm$ 0.02	7.92 $\pm$ 0.22	8.12 8.28
T ( $^{\circ}\text{C}$ )	15.70 $\pm$ 0.14	21.93 $\pm$ 1.85	38.5 42.2
Cond (mS/cm)	1.04 $\pm$ 0.06	1.50 $\pm$ 0.39	1.23 1.87
TDS (g/l)	0.4 $\pm$ 0.46	1.05 $\pm$ 0.28	1.12 1.27
$\text{Ca}^{2+}$ (meq/L)	1.52 $\pm$ 0.14	1.15 $\pm$ 1	0.215 0.75
$\text{Mg}^{2+}$ (meq/L)	1.16 $\pm$ 0.14	1.73 $\pm$ 1.17	0.145 0.162
$\text{Na}^+$ (meq/L)	6.93 $\pm$ 0.59	14.57 $\pm$ 2.31	8.9 16.65
$\text{K}^+$ (meq/L)	0.20 $\pm$ 0.02	0.21 $\pm$ 0.06	0.092 0.113
$\text{HCO}_3^-$ (meq/L)	7 $\pm$ 0.17	14.30 $\pm$ 3.15	7.14 13.99
$\text{SO}_4^{2-}$ (meq/L)	0.11 $\pm$ 0.001	0.34 $\pm$ 0.07	0.178 0.296
$\text{Cl}^-$ (meq/L)	2.72 $\pm$ 0.81	3.25 $\pm$ 0.35	2.45 3.66

Cond: conductivity, TDS: total dissolved solids.

### 3.3. Data analysis

The saturation index (SI) was calculated using the PHREEQC program (Parkhurst and Appelo, 1999), while the Base Exchange Index was calculated as follows:

$$\text{BEI} = \text{Cl}^- - (\text{Na}^+ + \text{K}^+) / \text{Cl}^- (\text{meq/L})$$

(Custodio, 1997).

## 4. Results and discussion

### 4.1. Groundwater

#### 4.1.1. Hydrochemical characteristics

The ionic composition of groundwater from the Chasicó locality is shown in Table 1.

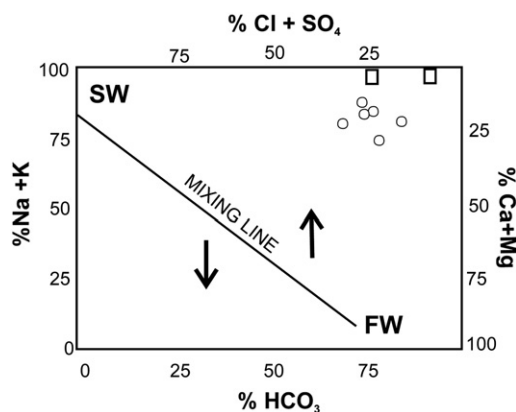


Fig. 3. Chebotarev diagram representing a hypothetical line of mixing between freshwater and sea water ( $\uparrow$  direct cation exchange;  $\downarrow$  inverse cation exchange). SW: sea water, FW: freshwater, white circles: groundwater from the Chasicó locality, white squares: groundwater from forest center Alexander Von Humbolt.

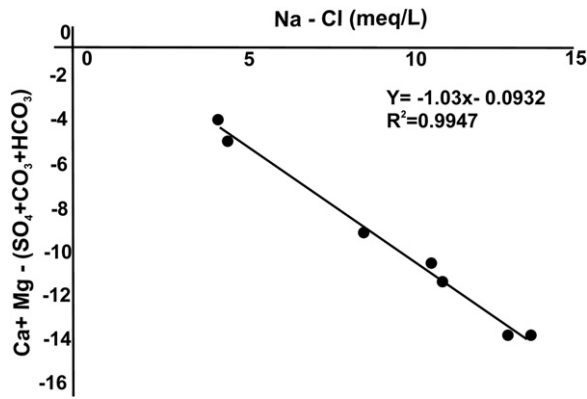


Fig. 4. Relationship between  $\text{Ca}^{2+} + \text{Mg}^{2+} - (\text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-})$  and  $\text{Na}^+ - \text{Cl}^-$  for the groundwater of the Chasicó locality.

Table 2

Physico-chemical parameters (mean values  $\pm$  standard deviation) of the surface water of the Chasicó Lake and Chasicó Stream, during wet and dry periods.

	Wet period		Dry period	
	Chasicó Lake	Chasicó Stream	Chasicó Lake	Chasicó Stream
pH	8.72 $\pm$ 0.04	8.59 $\pm$ 0.03	8.64 $\pm$ 0.05	8.60 $\pm$ 0.20
T (°C)	10.40 $\pm$ 0.14	11.89 $\pm$ 0.70	17.85 $\pm$ 1.68	13.67 $\pm$ 0.06
Cond (mS/cm)	38.75 $\pm$ 0.07	9.54 $\pm$ 0.06	44.48 $\pm$ 1.25	19.23 $\pm$ 0.15
TDS (g/l)	21.12 $\pm$ 0.05	6.62 $\pm$ 0.12	31.13 $\pm$ 0.88	13.43 $\pm$ 0.17
$\text{Ca}^{2+}$ (meq/L)	2.88 $\pm$ 2.55	4.71 $\pm$ 0.14	3.04 $\pm$ 0.89	2.07 $\pm$ 0.10
$\text{Mg}^{2+}$ (meq/L)	49.37 $\pm$ 0.07	7.81 $\pm$ 0.14	57.08 $\pm$ 1.32	22.18 $\pm$ 0.08
$\text{Na}^+$ (meq/L)	432.47 $\pm$ 20.93	93.26 $\pm$ 0.97	529.90 $\pm$ 39.7	171.97 $\pm$ 3.12
$\text{K}^+$ (meq/L)	4.99 $\pm$ 0.34	1.37 $\pm$ 0.05	9.43 $\pm$ 1.77	3.91 $\pm$ 0.14
$\text{HCO}_3^-$ (meq/L)	14.03 $\pm$ 3.08	7.90 $\pm$ 0.40	19.95 $\pm$ 2.04	10.41 $\pm$ 0.21
$\text{SO}_4^{2-}$ (meq/L)	0.93 $\pm$ 1.16	0.10 $\pm$ 0.01	0.80 $\pm$ 0.16	0.23 $\pm$ 0.01
$\text{Cl}^-$ (meq/L)	469.95 $\pm$ 18.46	99.20 $\pm$ 0.40	585.18 $\pm$ 22.69	182.75 $\pm$ 1.29
$\text{CO}_3^{2-}$ (meq/L)	ND	ND	14.36 $\pm$ 1.50	4.92 $\pm$ 0.18

Cond: conductivity, TDS: total dissolved solids, ND: non-determined.

The recorded pH values indicate that the sampled groundwater was slightly alkaline ( $<7.92$ ). The mean conductivity was 1.04 and 1.50 mS/cm in the wet and dry periods, respectively, while TDS was 0.4 and 1.05 g/L in the wet and dry periods, respectively (Table 1).

Sodium was the most abundant cation in the groundwater, with its concentration during the dry period being twice that during the wet period. Calcium and magnesium were less abundant and represented together less than 15.5% of total cation composition, while potassium represented less than 2% of total cation composition of groundwater (Table 1).

Bicarbonate was the most abundant anion, with its concentration being lower in the wet period ( $7 \pm 0.17$  meq/L) with respect to the dry period ( $14.30 \pm 3.15$  meq/L). The relative abundance of anions and cations in the groundwater from the Chasicó locality ( $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ ,  $\text{Na}^+ > \text{Ca}^{2+} + \text{Mg}^{2+} > \text{K}^+$ ) was equivalent to the one that was previously found in the groundwater of Bahía Blanca (in southwest Buenos Aires province), which is at 71 km far from Chasicó locality (Blanco et al., 2006). It is interesting that conductivity, TDS, pH and cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$ ) of the groundwater from forest center Alexander Von Humbolt were similar in the wet and dry periods.  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  had different concentrations between both periods, being higher in the dry period (Table 1). This would evidence that the precipitations may influence decrease the ionic concentration of the geothermal well for dilution effect.

#### 4.1.2. Cation exchange process

Groundwater chemical data obtained in the dry and wet periods were analyzed by means of the Chebotarev diagram (Fig. 3). The axes of the diagram show the percentages of bicarbonate ions (lower axis), chloride + sulfate (upper axis), sodium + potassium (left axis), and calcium + magnesium (right axis). A hypothetical line of mixing between freshwater and sea water (or marine sediments) is represented. The vertical deviations from the line of mixing may be attributed to direct and inverse cation exchange. As it can be seen in Fig. 4, groundwater samples has an increased percentage of  $\text{Na}^+ + \text{K}^+$  and decreased

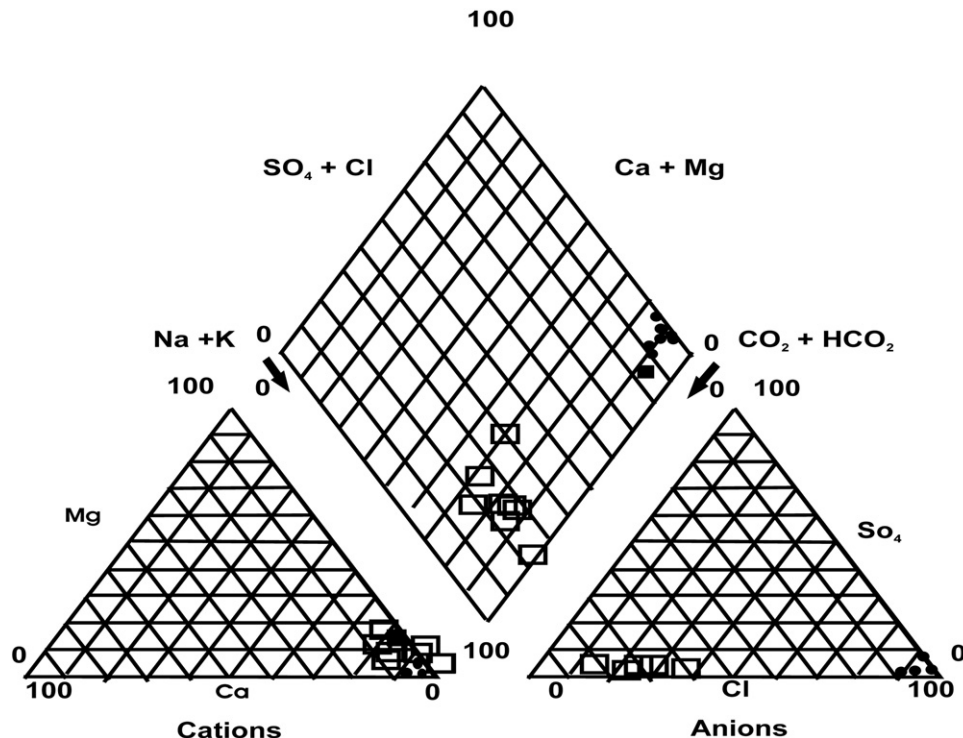


Fig. 5. Piper diagram showing the concentration of major ions (in meq/L) in surface water samples collected in the Chasicó Lake (black circles) and Chasicó Stream (black squares), and in groundwater samples (white squares).

**Table 3**

Mean salinity (g/L) and concentration of major ions (eq/L % of salinity) in sea water, some salt lakes, and Pampean shallow lakes.

Salt lake/sea	Salinity(g/l)	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	References
Seawater	35	77	2	4	18	90	9.3	0.4	–	Hem (1985)
Am-Ki (South America)	29	73.6	0.75	6.4	19.2	73	15.4	7.6	2.4	Conzonno and Uliberrana (2010)
Chasicó (South America)	26.1	84	1.4	0.6	9.1	94.2	0.1	3.3	2.6	This paper
South Africa	24.7	77.6	0.02	8.7	12	70.1	20.1	10	ND	Day (1993)
Van (Asia)	23	94.8	2.8	0.1	2.4	44.6	13.6	10.7	31.1	Kalff (2003)
Namibian (Africa)	20	81.2	2	7.4	9.4	87	11	2.2	ND	Day (1993)
Grande (South America)	10.2	69	0.7	2.3	28.1	88	8	2.8	1.6	Conzonno and Uliberrana (2010)
Pampean shallow lake	Salinity (g/l)	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	References
Salada Grande	6.6	75.5	3.8	1.9	18.9	80.3	6.2	8.9	4.5	Drago and Quirós (1996)
Chascomús	1.6	71.4	17.8	3.5	7.1	60.6	18.2	15.1	6.1	Miretzky et al. (2000)
Lobos	1.4	85	2.6	8	15	45	30	25	4.5	Mariñelarena and Conzonno (1997)
Cochicó	1.35	85	2	3.5	10	25	25	46.5	4	Drago and Quirós (1996)

percentage of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  with respect to the hypothetical line of mixing, which was based on the calculation made by Miretzky et al. (2001). This fact suggest a cation exchange process in groundwater.

To further confirm the cation exchange process,  $\text{Ca}^{2+} + \text{Mg}^{2+} - (\text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-})$  was plotted against  $\text{Na}^+ - \text{Cl}^-$  for the groundwater of the Chasicó locality. A good correlation was obtained with a slope ( $p = -1.03$ ) close to the theoretical value of  $-1$ , which confirms the cation exchange process between  $\text{Ca}^{2+}$  and  $\text{Na}^+$  (Fig. 4). The base exchange index (BEI) were between  $-0.31$  and  $-6$ , indicative of a higher  $\text{Na}^+$  concentration due to cation exchange capacity with clays. Infiltrated soils release  $\text{Na}^+$  and take  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from water, which becomes of the sodium type, with lower hardness. However, there should be consider other factors that may influence in the index as ionic balance, exchange rock-water and the water biomass.

The BEI was  $-2.67$  (wet period) and  $-3.57$  (dry period) for the groundwater of forest center Alexander Von Humbolt, and  $-1.62$  (wet period) and  $-3.55$  (dry period) for the groundwater of the Chasicó locality. These results indicate that the sampled groundwater was saturated with  $\text{Na}^+$  due to cation exchange process.

This process was first described in the Salado Basin by Fernández Cirelli and Miretzky (2004) in Pampean plain, to assess the relationship between surface and groundwater.

#### 4.2. Surface water.

##### 4.2.1. Hydrochemical characteristics

The salinity and ionic composition of the surface water of the Chasicó Lake and Chasicó Stream are shown in Table 2.

The pH values recorded both in the dry and wet periods are indicative of alkaline water. The mean conductivity and TDS were higher in the Chasicó Lake than in the Chasicó Stream in both periods. These

parameters, as well as the concentration of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$ , differed considerably between the dry and wet periods (Table 2), which may be associated with climatic factors such as precipitation and evaporation. In particular, the lower conductivity and TDS recorded in the wet period, when rainfall was higher (289 mm accumulated rainfall in February–March 2010, according to the National Meteorological Service), may be due to a dilution effect. In order to classify the surface water of the Chasicó Lake and Chasicó Stream, their cation-anion compositions were plotted on Piper's trilinear diagram, which showed that is sodium chloride type (Fig. 5). This also occurs in pampean shallow lakes of South-America, except in Cochicó Lake that presents bicarbonate sodium water type (Table 3). The waterbodies of Africa and Asia were reported by Day, (1993) and Kalff (2003) as sodium chloride type (Table 3).

Pampean shallow lakes are chemically characterized by high concentrations of  $\text{Na}^+$ , soluble halides and bicarbonates. Their waters are consequently of the sodium bicarbonate or sodium chloride bicarbonate type, with no dominant anions, salinity lower than 3 g/L and high

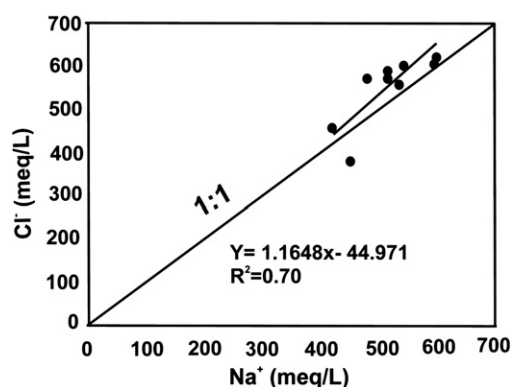


Fig. 7. Relationship between  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations (meq/L) for surface water of the Chasicó Lake.

**Table 4**

Saturation index for calcium carbonate in surface water of the Chasicó Lake and Chasicó Stream, and in groundwater from the Chasicó locality and forest center Alexander Von Humbolt, during wet and dry periods.

		Wet period	Dry period
Surface water	Chasicó Lake	$0.46 \pm 0.22$	$0.77 \pm 0.07$
	Chasicó Stream	$0.48 \pm 0.32$	$0.82 \pm 0.15$
Groundwater	Forest Center	0.19	0.6
	Chasicó Village	$0.053 \pm 0.04$	$0.33 \pm 0.26$

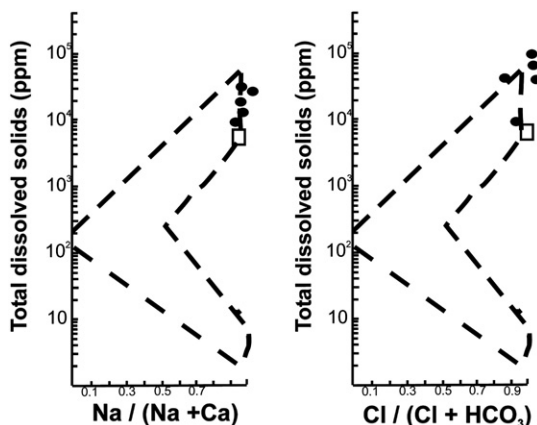


Fig. 6. Gibbs diagram for (a) cations and (b) anions.



**Table 5**

Arsenic (As), fluoride (F) and vanadium (V) concentrations (mean values  $\pm$  standard deviation) in surface water of the Chasicó Lake and Chasicó Stream and groundwater from the Chasicó locality, during wet and dry periods.

	mg/L	Wet period	Dry period	Wet period	Dry period
		Chasicó Lake		Chasicó stream	
Surface water	As	0.235 $\pm$ 0.251	0.242 $\pm$ 0.043	0.096	0.148
	F	7.54 $\pm$ 1.36	8.5 $\pm$ 0.02	6.74	6.77
	V	0.058 $\pm$ 0.024	0.231 $\pm$ 0.19	0.068	0.184
Groundwater	mg/L	Wet period		Dry period	
	As	0.066 $\pm$ 0.057		0.093 $\pm$ 0.002	
	F	2 $\pm$ 0.02		1.97 $\pm$ 1.2	
	V	0.273 $\pm$ 0.006		0.301 $\pm$ 0.176	

hardness (oversaturation for calcite and dolomite) (Conzonno, 2009; Fernández Cirelli and Miretzky, 2004; Miretzky et al., 2000, 2001).

The relative contribution of major cations to total cation composition of surface water of the Chasicó Lake and Chasicó Stream was: >86% for sodium, <1% for calcium and potassium, and >7.31% for magnesium. These results are in agreement with previous findings in Pampean shallow lakes (Fernández Cirelli and Miretzky, 2004). Chloride was the most abundant anion in surface water of the Chasicó Lake and Chasicó Stream. Its concentration was lower in the wet period ( $469.95 \pm 18.46$  meq/L in the Chasicó Lake, and  $99.60$  meq/L in the Chasicó Stream) with respect to the dry period ( $585.18 \pm 22.69$  meq/L in the Chasicó Lake, and  $224.60$  meq/L in the Chasicó Stream). Bicarbonate tended to increase during the dry period in both water bodies.

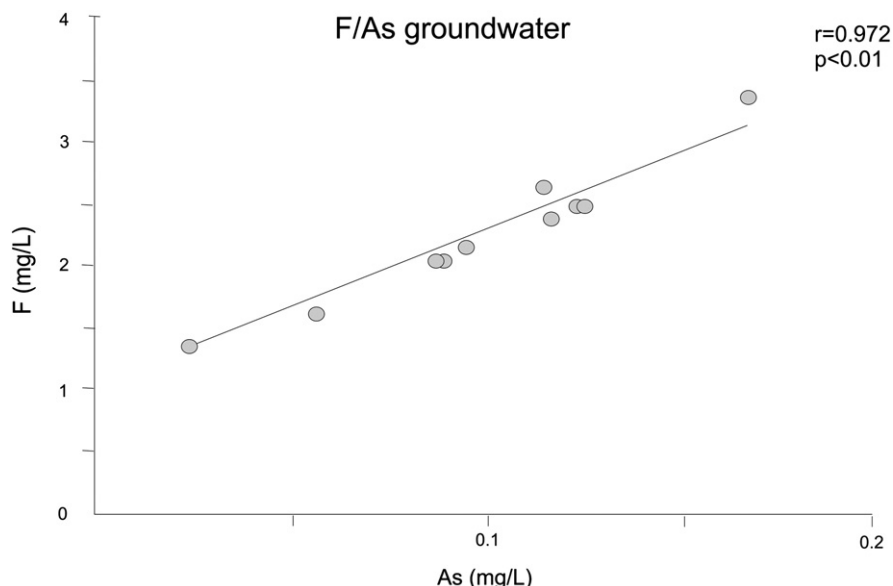
The concentration of major ions in the Chasicó Lake was higher than that in the Chasicó Stream during both periods (Table 2). This may be due to the fact that the lake receives water from the stream and runoff from the surrounding land since it is located in a depressed area ( $\sim 20$  m a.s.l.), and to the salt resolubilization that may occur during wet periods. Hence, the differential precipitation of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  as a result of evaporative concentration at high salinities appears to be determinant of the relative abundance of major ions in these systems, with water being enriched in  $\text{Cl}^-$  and  $\text{Na}^+$ .

Present results agree with those reported by Kilham (1990) showing that  $\text{Na}^+$  and  $\text{Cl}^-$  are probably the main ions in most salt lakes worldwide. Moreover, sodium chloride was demonstrated to be the dominant salt in some salt lakes over the world (Day, 1993; Kalff, 2003). This may

be the result of the high relative solubility of NaCl. The same occurs in Pampean shallow lakes, but the concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  in these lakes are lower (Table 3). Conzonno and Uliberrana (2010) analyzed the hydrogeochemistry of lakes from Tierra del Fuego province (Argentina). The presence of ancient salts in two of the shallow lakes studied, Am-Ki and Grande, reflects their origin in the sea ingressão/regression that occurred during the Quaternary age, and determines a high salinity of sodium chloride type. The same may be applied to Chasicó Lake. Even though  $\text{Na}^+$  is the dominant cation in most inland salt lakes, they are typically characterized by both a dominant and a sub-dominant anion ( $\text{Cl}^-$  and  $\text{HCO}_3^-$ , respectively). The Pampean lakes are eutrophic or hypertrophic (Schenone et al., 2008) and they are sodium bicarbonate or sodium chloride type with no dominant anion (Drago and Quirós, 1996; Miretzky et al., 2000).

#### 4.2.2. Cation exchange process

According to Gibbs (1970), three natural mechanisms influence the chemistry of surface water: atmospheric precipitation, rock dominance or rock weathering, and the evaporation-crystallization process. The cationic Gibbs diagram, a boomerang-shaped envelope, was obtained when the  $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$  ratio on the x axis was plotted against TDS values on the y axis (Fig. 6A). This diagram has been used by Miretzky et al. (2001) in the study of Pampean shallow lakes. Its analysis allows determining water chemical composition is controlled by precipitation rather than rock weathering.



**Fig. 8.** Correlations between As/F in groundwater.

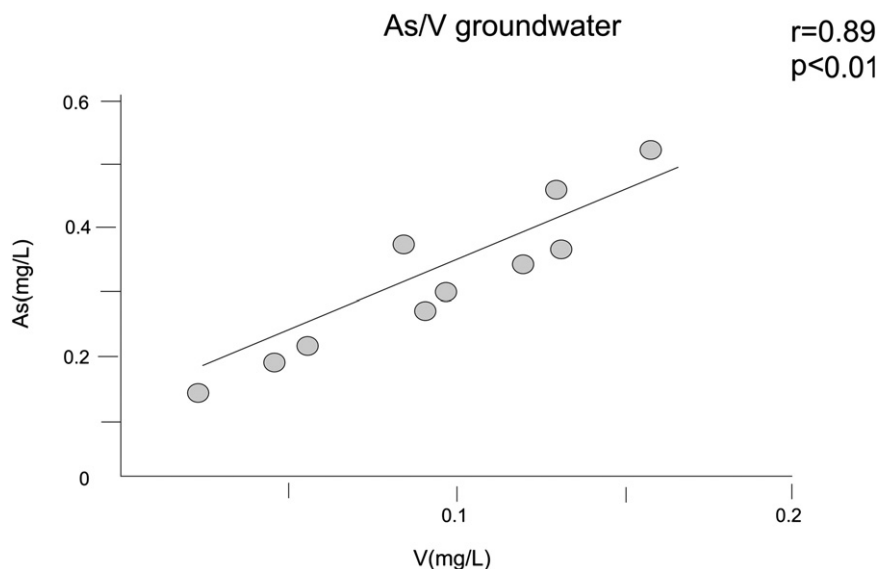


Fig. 9. Correlations between As/V in groundwater.

Data of surface waters whose chemical composition is influenced by precipitation are plotted in the lower right side of the boomerang-shaped envelope (low values of TDS and high values of  $\text{Na}^+$  / ( $\text{Na}^+ + \text{Ca}^{2+}$ ) ratio) (Gibbs, 1970). When rock weathering is the main process controlling the chemistry of surface water, calcium and bicarbonate are the main ions, TDS values are moderate, and data are plotted in the central region of the boomerang-shaped envelope. On the other hand, the evaporation–crystallization process is important in arid and template areas, where evaporation exceeds the amount of precipitation and the water chemical composition is similar to that of sea water. Data of surface water whose chemical composition is influenced by this process are plotted in the upper right side of the boomerang-shaped envelope, in a continuous series between surface water whose chemical composition is controlled by climatic conditions and evaporation. However, Fernández Cirelli and Miretzky (2004) obtained different results in a Pampean shallow lake (Chascomús), where the relative abundance of cations and anions was in the order  $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$  and  $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$ , respectively.

There are many deviations from this scheme in the Southern Hemisphere (Day, 1993; Eilers et al., 1992; Kilham, 1990; Miretzky et al., 2001; Wetzel, 2001). However, the surface water of the Chasicó Lake does not deviate from the Gibbs cationic diagram (1970), with its chemical composition being similar to that of sea water and other salt lakes of Patagonia (Conzonno and Uliberrana, 2010), Kenya and India (Njenga, 2004) (Fig. 6A).

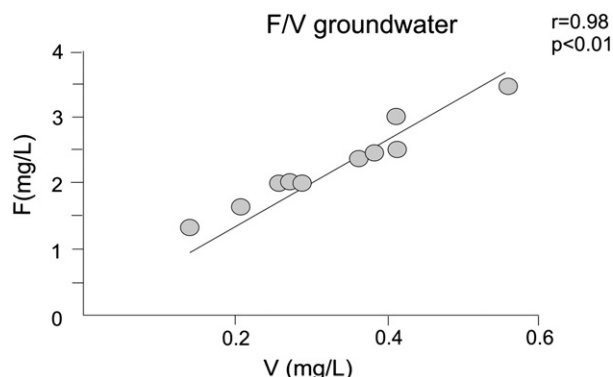


Fig. 10. Correlations between F/V in groundwater.

On the other hand, the Gibbs anionic diagram was obtained when the  $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$  ratio on the x axis was plotted against TDS values on the y axis (Fig. 6B). It was in agreement with the Gibbs cationic diagram, and showed that the chemical composition of the Chasicó Lake is close to that of sea water, and is mainly controlled by the crystallization–evaporation process. This is associated with the high salinity of the lake, which is similar to that of sea water ( $>33$  g/L) (Stumm and Morgan, 1970). On this basis, the Chasicó Lake may be classified as a salt lake (10–100 g/L) or as a polyhaline lake (16–40 g/L), according to Gorrel (1958); Ringuelet (1962), respectively.

The relative abundance of cations in sea water is in the order  $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ , while that of anions is in the order  $\text{Cl}^- > \text{SO}_4^{2-}, \text{HCO}_3^-$  (Goldberg et al., 1971). Similar results were obtained in the present study for the Chasicó Lake, which may be a consequence of the dissolution of ancient salts, as a result of sea ingressions and transgressions occurring in that area during the Querandinese period (Cenozoic) (Nicolli et al., 2007). In particular, the concentration of  $\text{Cl}^-$  is in the same order of magnitude and correlates with the concentration of  $\text{Na}^+$  in the surface water of the Chasicó Lake (Fig. 7), similarly to what happens in sea water (Table 2). Besides, monovalent ions ( $\text{Na}^+$  and  $\text{Cl}^-$ ) prevail over divalent ions ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ), probably as a result of calcite and dolomite precipitation (Njenga, 2004).

With respect to the saturation index, all samples showed saturation for calcite ( $\text{SI} > 0$ ), which indicates possible precipitation of this mineral phase (Table 4). The values of SI calcite in Chasicó Lake in the dry period are higher than in the wet period. During the summer decreases the solubility of  $\text{CO}_2$  in the water because of the high temperatures and the photosynthetic activity. These two processes elevate the pH level of the water so that calcium carbonate precipitates.

SI for calcite was higher in the Chasicó Stream in both periods. This is probably due to the evaporation process that increases the concentration of salts in solution, and has a greater effect on the stream.

Present results showing a different chemical composition of surface water and groundwater suggest that, unlike what happens in the typical Pampean shallow lakes (Fernández Cirelli and Miretzky, 2004), groundwater should not be the main source of water of the Chasicó Lake.

Moreover, the BEI of surface water ranged between 0.04 and 0.08 in both periods, indicating that the cation exchange process is not dominant, in spite of its importance for the geochemical processes that determine the composition of water in typical pampasic ponds.

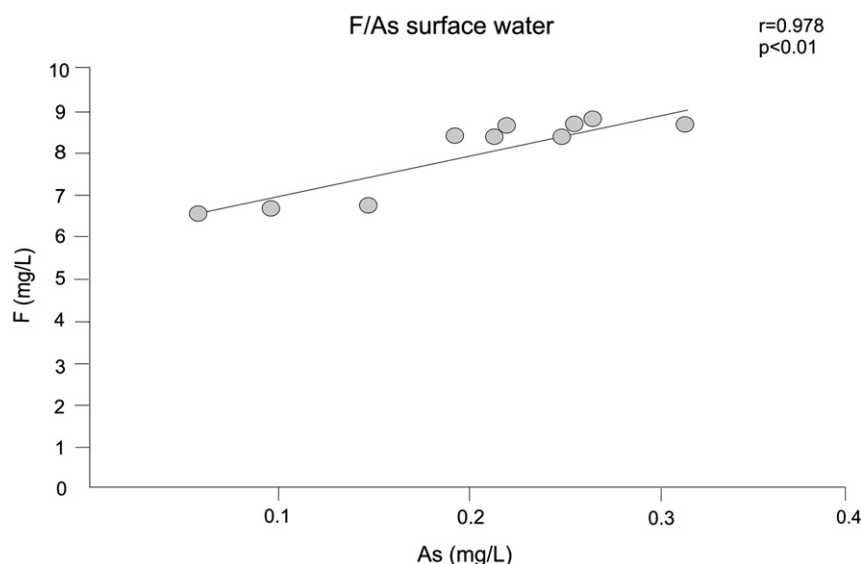


Fig. 11. Correlations between As/F in surface water.

#### 4.3. Arsenic, vanadium and fluoride in surface water and groundwater.

As, F and V concentrations determined in Chasicó Lake, Chasicó stream and groundwater from the neighborhood in the studied period are shown in Table 5. Significant correlations were found as expected in groundwater between: (1) As and F in ( $r = 0.99$ ,  $p < 0.05$ ) (Fig. 8); (2) As and V in groundwater ( $r = 0.99$ ,  $p < 0.05$ ) (Fig. 9); and (3) V and F in groundwater ( $r = 0.99$ ,  $p < 0.05$ ) (Fig. 10), while in surface water it was only found for As and F ( $r = 0.91$ ,  $p < 0.05$ ) (Fig. 11). V was concentrated in Chasicó Lake as a consequence of the evaporation process in the dry period. As and F have similar concentrations in both periods (Table 5). This can be because in the wet period precipitations may increase the weathering of the minerals around the lake and as a consequence of the run-off they get inside the waterbody. In the case of V, it has a lower concentration during the wet period possibly due to the run-off process. The Chasicó stream has lower concentrations of As, F and V than the lake in all the periods. That may be probably because it is a lotic body. In addition, these elements behave in a similar way to that in the lake. There are similar concentrations of As and F in both periods meanwhile there are lower concentrations of V in the wet period. As and F values were lower in groundwater than in surface water, while V concentrations were higher. As, F and V were similar in groundwater in both periods. The As, F and V concentration values were higher and more widely dispersed in surface water than in groundwater, as a consequence of evaporation. The fact that these elements do not correlate in surface water may also indicate a different origin. The presence of As, F and V in Chasicó Lake is not the result of anthropic pollution since there are not sources of industrial pollution, so the origin of these elements is from volcanic glass from Pampean loess. It cannot be assured that these elements are derived from groundwater since no connection between these two water sources has been found (Puntoriero et al., 2014).

## 5. Conclusions

Differences in the physico-chemical parameters of the Chasicó Lake in relation to other shallow lakes of the Pampean plain may be explained by their different geomorphological origins.

Present results confirm that one of the factors controlling groundwater composition is the cation exchange process.

The chemical composition of surface water of the Chasicó Lake differed significantly from that of groundwater, which suggests that the latter is not the main source of water of the former.

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