Ionic relations: a tool for studying hydrogeochemical processes in Pampean shallow lakes (Buenos Aires, Argentina)

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Abstract

Main geochemical processes that determine the chemical composition of shallow lakes in the lower Salado River basin were studied. The region is characterized by the total lack of slope and the succession of humid and dry climates where the lakes are shallow alkaline and eutrophic ecosystems, with circulation pattern corresponding to polymictic lakes. Gibbs classical diagrams confirmed that weathering of mineral phases and evaporation-crystallization were the principal processes involved. Nevertheless, deviations to the basic pattern were observed. The study of ionic relations (in $meq\,l^{-1}$) determined that a cationic exchange process takes place in the Pampean loessic sediments, influencing the chemical characteristics of both groundwater's and surface waters.
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1. Introduction

The Chaco-Pampa plain is one of the most extended plain regions of the world. Climate, as well as its geomorphology, results in the development of wetland systems and very shallow lakes (Iriondo, 1989), which play an important role in the overall hydrological cycle of Buenos Aires Province (Southern Pampa). The lack of slope is responsible for the disparity between the abundance of lentic water bodies (1429 lakes with 500 m length, Gómez and Toresani, 1998) and the low density of the drainage net. They have several functions, among them charge and discharge of aquifers, flood control, water provision, climate regulation, recreational use, sportive fishing, and waste disposal.

Pampean shallow lakes have different origins related to climate changes at the end of the Quaternary Age (Dangavs, 1998), but without lakes as predecessors. The principal ones are deflationary by eolian action, tectonic action, or abandoned fluvial beds, isolated lagoons, and old estuaries. Their degree of salinity is varied, ranging from oligohaline to hyperhaline. The salt concentration observed is caused by marine ingressions, and the sedimentary and climatic characteristics of the Pampa Deprimida (center-east of the Buenos Aires Province).

Chemical compositions include sodium chloride bicarbonate or sodium bicarbonate chloride type, oligosulphate to sulphate type, and hypomagnesium to hemimagnesium type.

These lakes are shallow alkaline ecosystems, with circulation patterns corresponding to polymictic lakes. This indicates nearly continuous vertical mixing that promotes a high concentration of suspended particulate matter and low transparency. The water column is almost always thermally homogeneous, saturated with dissolved oxygen and with a high content of dissolved organic matter, mainly humic substances (Conzonno and Fernandez Cirelli, 1987, 1988), with aquatic macrophytes at different development stages. They show a typical profile of pfanne or wanne with a shoreline development less than 4 indicating simple geometrical figures, and a maximum depth of 4 m. Upper sediments are sandy silt, silt and clayey silt, with a calcium carbonate content between 1% and 20%, and organic matter lower than 15%. Nutrient concentrations (phosphorus and nitrogen) as well as organic matter, phytoplankton biomass, presence of aquatic macrophytes, algae blooms and fish community indicates that these ecosystems were eutrophic (Ringuelet, 1962; Quirós and Drago, 1999).

The local groundwater drainage is the basic discharge of Pampean lake waters (Sala et al., 1983). During flood periods, water is stored in depressions forming shallow lakes and marshes, and that exceeding the storage

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capacity of the depressions moves very slowly through the surface as sheet flow. Infiltration is very important due to the regional lack of slope ($0.3 \, \text{m km}^{-1}$) and the soil characteristics, and thus the water table is near the surface in most places.

Because of their shallowness, the dynamics of Pampean lakes are intricately tied to climate conditions, and the annual precipitation and evaporation volumes are of the same order of magnitude as their hydric volumes. In spite of the alternation of humid and dry multiannual periods, many of them are permanent and attain a steady state. Changes in the hydrological cycle caused by climatic conditions or by anthropogenic activities can have a large impact on the water level and hydrochemistry of these lakes. For example, Chascomús shallow lake was sampled monthly from May 1999 to May 2000, being the annual precipitation–evaporation balance positive (508.7 mm) for the sampling period, even though it was negative in spring and summer promoting a ca. 60% decrease in the lake's mean water level (from 1.98 m to a minimum value of 1.15 m). Precipitation was highest in April and May 2000, and water level increased ca. 76%, showing a strong dependence of this shallow lake on climatic conditions. During the sampling period, pH was always alkaline (mean value 9.11, range 8.41–9.61). Total dissolved solids (TDS) varied by more than a factor of two (mean value $1548 \, \text{mg} \, \text{l}^{-1}$, range $821–1972 \, \text{mg} \, \text{l}^{-1}$) and total suspended solids (seston) by a factor of three (mean value $102 \, \text{mg} \, \text{l}^{-1}$, range $55–145 \, \text{mg} \, \text{l}^{-1}$). Carbonates increased by the displacement of carbonate/bicarbonate equilibrium owing to high temperatures and photosynthetic activity during the summer, and dissolved silica decreased when consumed by growing diatom populations, mainly in spring and summer. The other analyzed hydrochemical variables (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, pH, and COD) also increased in summer due to evaporation processes linked to water level decrease and temperature increase (Miretzky et al., 2002).

A primary objective of geochemistry is to understand the behavior of systems based on knowledge of its basic properties. One of the significant legacies that Stumm and Morgan (1996) provided the field of aquatic chemistry is the notion that geochemical phenomena can be understood through the investigation of models, with lakes as better "test tubes". Our studies concern the principal geochemical processes that determine the chemical composition of the shallow lakes, particularly those situated in the Salado River drainage basin.

2. Study area

The lower Salado River drainage basin ($35°17'–36°00'$S and $59°07'–57°40'$W) is located in the geomorphic unit called Pampa Deprimida, in the center-east of Buenos Aires Province. The geological characters are those of the low topographic slope great plain areas (Auge and Hernandez, 1983): surface geologic monotony; little tectonic deformation; predominance of fine sediments (clays and silts) over coarse ones (sand sediments), and continuity and areal extension of the geological units. The Salado basin is a sedimentary basin where Cretaceous, Tertiary (lower and upper), Plio-Pleistocene and Pleistocene (Middle and Upper) sediments are superimposed over the Precambrian crystalline basement. The Pampean sediments or Pampean loess (Middle and Upper Pleistocene) are of special importance in the chemical composition of the groundwater. These sediments have generally been regarded as aeolian in origin, being derived from volcaniclastic deposits outcropping in the Andes over 1000 km to the west (Iriondo, 1997), although localized fluvial and mass movement processes probably redistributed the material once accumulated in the Pampean region to a large extent (Iriondo and Kröhling, 1996; Iriondo, 1999).

Pampa Deprimida has a wet climate and a mean temperature between 13°C and 16°C. Mean annual precipitation (1961–1990) was between 850 and 950 mm. Although precipitation is high in the summer, the precipitation–evaporation balance is usually negative in this season. The region is characterized by a very gentle slope ($0.3 \, \text{m km}^{-1}$) and extremely low morphological potential that makes the runoff difficult during flooding periods. Infiltration and evapotranspiration are the principal hydrological cycle components.

The Salado River is the most important river of the Buenos Aires Province. It flows along a NW–SE axis, meanders through a floodplain covered with shallow lakes and marshes that supply water to the river or receive water from it depending on their respective hydrological levels and joins the River Plate Estuary in Samborombón Bay, which has the characteristics of a marine environment. The Salado River length is 690 km and its catchment area is about $80,000 \, \text{km}^2$ (Ringuelet, 1972). It is a typical river of Southern Pampa plain, with a slow regime and variable flow (maximum historical discharge: $1006.31 \, \text{m}^3 \, \text{seg}^{-1}$, 1998 mean value $25.6 \, \text{m}^3 \, \text{seg}^{-1}$ at Junín City). It presents a meandering pattern, especially in the lower section, and tributaries in the left bank.

Channel 15 and several minor channels are the only artificial drainage in the area. In flooding periods, the situation is critical because of the total lack of slope and the high Salado River flow.

The main shallow lakes in the lower Salado River drainage basin are: Lobos ($35°17'$S; $59°07'$W), San Miguel del Monte ($35°27'$S; $58°48'$W) and the "Encadenadas de Chascomús" system that includes Vitel ($13 \, \text{km}^2$), Chascomús ($35°36'$S, $58°02'$W) ($30 \, \text{km}^2$), Adela ($21 \, \text{km}^2$), Manantiales, del Burro ($10.7 \, \text{km}^2$), Chis Chis ($14.8 \, \text{km}^2$), Tablilla ($16.7 \, \text{km}^2$) and Las Barrancas

($8.85 \, km^2$). They are intercommunicated by rivers and are connected with the Salado River through the La Horqueta River (Fig. 1).

3. Materials and methods

The "Encadenadas de Chascomús" system sampling has been previously described (Miretzky et al., 2000; Miretzky et al., 2001a). Surface and shallow ground-water samples from Lobos Lake and its tributaries and from wells used by rural population for human and cattle comsumption were collected during August 1998. The samples were filtered using $0.45 \, \mu m$ acetate cellulose membrane (Micro Separations Inc., MSI), and were stored in polyethylene bottles.

Temperature and pH were determined in the field by means of a portable pH meter (Hanna HI 9025). Major ions were determined by conventional methods (APHA, 1993): carbonates and bicarbonates by acid titration, chloride by $AgNO_3$ titration, and sulphate by precipitation titration with $BaCl_2$ using sodium rodizonate as an indicator in water-acetone medium. Na and K were determined by atomic spectrophoto-metric emission, and Ca and Mg by atomic spectrophotometric absorption (Varian Techtron Model AA275).

Determinations were performed in duplicate, with relative errors $<1.0\%$ for all. The accuracy of the analysis for major ions was estimated from the electro-neutrality condition (Appelo and Postma, 1993). Total dissolved solids (TDS) were calculated as the sum of the above ion concentrations. Saturation indexes were calculated using the computer program WATEQF (Plummer et al., 1978).

Three loess samples were taken from a *calicata,* considering the Chascomús Soil Map 3557-5 (INTA, 1998) and analyzed by optical microscopy at the Departamento de Geología, Universidad de Buenos Aires and by X-ray diffraction, at the Centro de Investigaciones en Suelos y Aguas (CISAUA) - Centro de Investigaciones Geológicas (CIG), Universidad Nacional de La Plata. The chemical percent composition of the loess was determined at the Departamento de Geología, Universidad de Buenos Aires applying Shapiro's method (Shapiro, 1975). Once the loess samples were attacked, Na_2O, K_2O, CaO, and MgO were determined in a similar way as the water samples. SiO_2 Al_2O_3 Fe_2O_3 TiO_2 P_2O_5 and MnO_2 by spectro-photometric determination (1 cm path length Jasco 7850 spectrophotometer) after complexing with ammonium molybdate and reduction with 1-amino-2 naphthol-4 sulfonic acid ($\lambda = 815 \, nm$), alizarin S ($\lambda = 475 \, nm$), o-phenantroline ($\lambda = 560 \, nm$), tirón ($\lambda = 420 \, nm$) respectively, P_2O_5 by the blue phosphomolibdic complex after reduction with ascorbic acid ($\lambda = 815 \, nm$), and MnO_2 by oxidation to MnO_4^- with KIO_4 ($\lambda = 525 \, nm$). H_2O^- was determined at $105°C$ and H_2O^+ at $1200°C$. CO_2 was determined by volumetric titration. Determinations were performed in duplicate, with relative errors $< 1.0\%$.
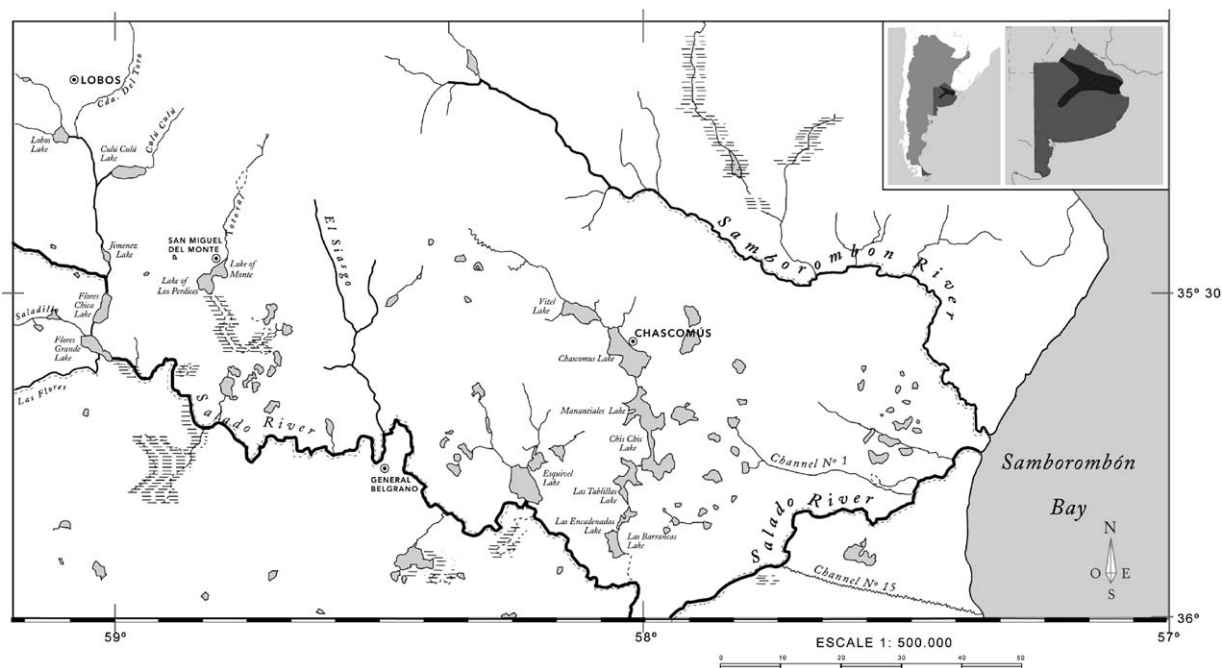

Fig. 1. South America, Argentina, Buenos Aires Province, Salado River lower drainage basin.

4. Results and discussion

The first environment studied in the Salado River drainage basin was the "Encadenadas de Chascomús" system. Surface waters were alkaline (pH mean value 8.30; range 6.80–10.33) and TDS mean value was 1447 ppm (range 744–2388 ppm), a larger value than the world mean value of $120 \, mg \, l^{-1}$ (Livingstone, 1963). Water chemical composition is shown in Fig. 2. Ionic composition was strongly alkaline ($>75\%$ meq l^{-1} $Na^+ + K^+$) with no dominant anion type. Composition of mean continental water (Livingstone, 1963) shows (meq l^{-1}) $Ca^{2+} > Mg^{2+} > Na^+ > K^+$, and $HCO_3^- > SO_4^{2-} > Cl^-$. Nevertheless, our results were very different, as Na^+ is the principal cation, $Mg^{2+} > Ca^{2+}$, and $Cl^- > HCO_3^- > SO_4^{2-}$.

An important tool to analyse geochemical processes is the Gibbs (1970) diagram. Gibbs studying the salinity of world surface water concluded that three natural mechanisms control the chemistry of surface waters: atmospheric precipitation, rock dominance or rock weathering, and evaporation–crystallization process. Gibbs' diagram, a boomerang-shaped envelope, is obtained when the weight ratio $Na^+/(Na^+ + Ca^{2+})$ on the x axis is plotted vs TDS values on the y axis.

When the dominant process is rock weathering, waters produce calcium and bicarbonate as predominant ions, TDS values are moderate, and sample data plot in the middle region of the Gibbs boomerang. Low salinity waters of sodium chloride type are due to the atmospheric precipitation process and sample data plot in the lower right corner of the boomerang. The processes mentioned above do not exclude each other, and many surface waters present chemical composition between the two extremes. It seems better to consider rock weathering and atmospheric precipitation as the ends of a continuous series.

The third mechanism that controls the surface water chemistry is the evaporation–crystallization process, important in arid areas, where evaporation is larger than precipitation. The evaporation process increases TDS and the relation $Na^+/(Na^+ + Ca^{2+})$, the latter

principally due to calcite precipitation. The surface waters that respond to this process are on the right-upper side of the Gibbs boomerang in a continuous series between those whose chemical composition is derived from rock weathering and seawater composition.

When the weight relation $Na^+/(Na^+ + Ca^{2+})$ was plotted against TDS values for the "Encadenadas de Chascomús" system waters under study, it was observed that data lay outside the boomerang. $Na^+/(Na^+ + Ca^{2+})$ values lay between 0.9 and 1.0 and TDS values between 1.0 y $2.0 \, g \, l^{-1}$ (Fig. 3a). This fact means that rock weathering and evaporation-crystallization processes alone are unable to explain the chemical characteristics of surface waters. Also, no data plot in the lower-right side of the boomerang, meaning that atmospheric precipitation was not an important process in determining the chemical composition of these waters, although the hydrological balance was positive in this region.

Drago and Quirós (1996) in their report of the hydrochemistry of inland waters in Argentina found deviations from the Gibbs basic pattern. They concluded that chemical composition is largely controlled by rock weathering and by evaporative concentration, and deviations were due to dissolution of ancient marine salts. Since the amount of Na^+ (meq l^{-1}) was larger than that of Cl^- (meq l^{-1}), the dissolution of ancient salts of marine origin could not be the only explanation of the deviations from Gibbs diagram, since halite dissolution would provide equal amounts of both ions.

In order to explain the origin of the excess of Na, a plot of $Ca + Mg—(SO_4 + HCO_3 + CO_3)$ against $Na–Cl$ was performed. Results indicated a good linear correlation ($R^2 = 0.94$) and a slope (-0.95) that tends to the theoretical value of -1. This behavior may be explained considering an ion exchange reaction in the hydrochemical evolution as Fisher and Mullican (1997) observed in groundwater of the Chihuahuan Dessert (Texas, USA). Therefore, we proposed that a cation exchange process took place in the Pampean loessic sediments, not previously described in this region (Miretzky et al., 2000).

Pampean loess chemical composition in the study area is shown in Table 1. Taking into consideration % Na_2O, % K_2O and % SiO_2 values, Pampean loess presents a dacitic chemical composition. In the sandy fraction, the acid mesosilicic volcanic lithic fragments constitute 39% of the felsic suite, the volcanic glass 22%, plagioclases 25%, quartz 7% and potassium feldspar 7%. The heavy components constitute a mafic suite, and represent only 0.4% of the sand fraction, the principal components being: amphiboles (hornblende) 25%, pyroxene (hypersthene and augite) 33%, opaque minerals (magnetite, hematite, ilmenite) 29%, basic lithic volcanic fragments (andesites and basalts) 4%, epidote 6%, and zircon, rutile and mica 3%. A X-ray study of the clay
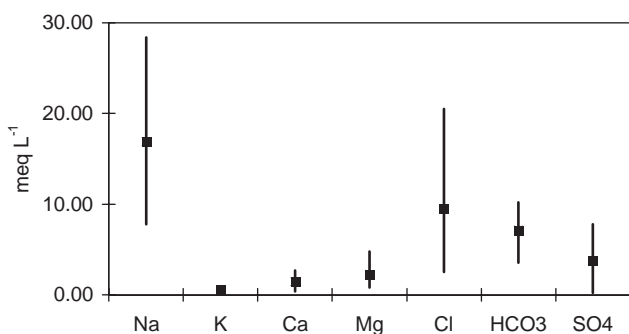

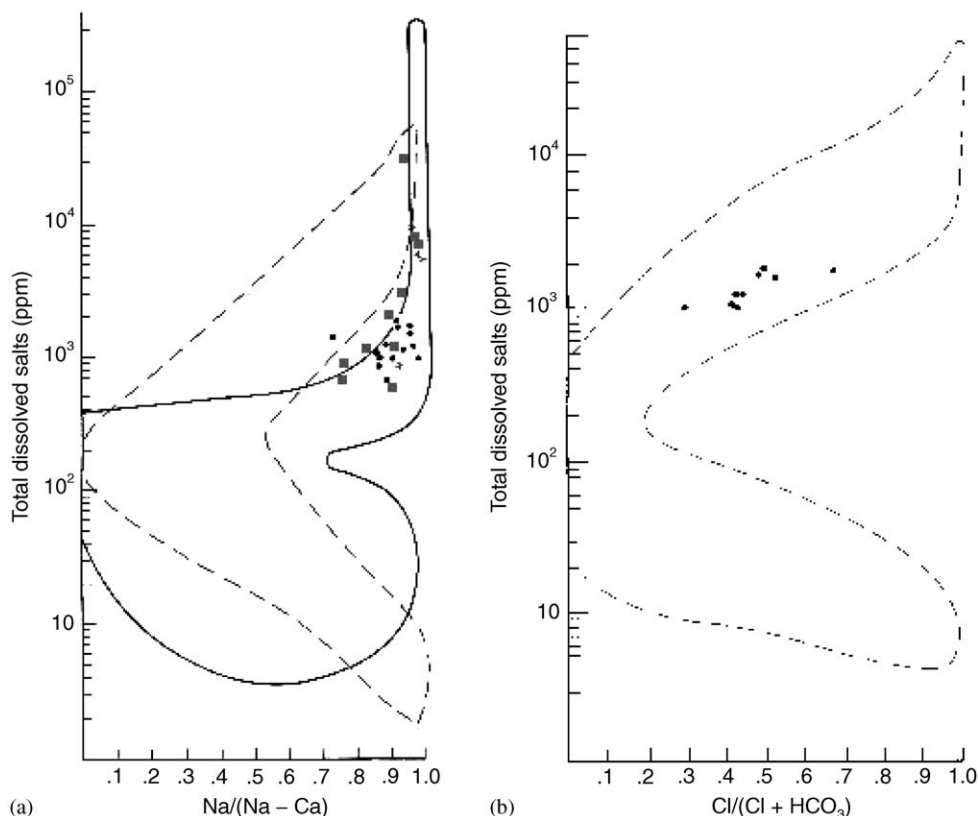Fig. 2. "Encadenadas de Chascomús" system chemical composition of surface water.

Fig. 3. Gibbs diagram "Encadenadas de Chascomús" system: (a) cationic, (b) anionic.

Table 1
Pampean loess chemical composition of three samples in "Encadenadas de Chascomús" region

S	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	MnO (%)	P_2O_5 (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	H_2O^+ (%)	H_2O^- (%)	CO_2 (%)
CH2	60.9	14.51	6.00	0.60	0.05	0.20	1.34	2.95	2.83	2.28	2.72	2.28	3.05
UD2	63.4	14.15	5.99	0.59	0.06	0.20	1.35	2.56	2.88	2.55	1.90	3.22	2.04
Abb	60.5	12.83	6.95	0.69	0.11	0.10	1.64	2.34	2.70	2.15	2.26	4.51	2.40

fraction reveals a montmorillonite content of 30%, illite 50%, interlayer illite-smectite 10%, chlorite 5% and kaolinite 5% (Miretzky et al., 2001b).

When a sodium clay (montmorillonite cation exchange capacity = 80 meq/100 g; Brady and Weil, 2001) interacts with a solution in which calcium is the predominant ion, each couple of absorbed sodium ions is replaced by a solubilized calcium, which enriches groundwater in sodium, thus changing it from a calcium bicarbonated type, into a sodium bicarbonated type. Therefore, when groundwater reaches the lakes, these being the main sources, lake waters become enriched in sodium. This process increases the weight relation $Na^+/(Na^+ + Ca^{2+})$ values and data plot outside the Gibbs boomerang.

On the other hand, the weight relation $Cl^-/(Cl^- + HCO_3^-)$ (x axis) was plotted against TDS values

(y axis) for Pampean lake waters (Fig. 3b). Gibbs' anionic diagram shows that data plot inside the boomerang shape envelope in the upper side, being rock weathering and evaporation–crystallization processes the ones controlling hydrochemistry. No data plot in the lower-right side of the boomerang, where chemical composition is determined by atmospheric precipitation process. The evaporation–crystallization process increases TDS and promotes calcite precipitation. If the dissolution of ancient salts of marine origin was the process determining the deviation from the Gibbs basic pattern, this deviation should also be observed in the anionic diagram.

The Gibbs diagram is a very important tool to determine geochemical processes. Nevertheless, the study of the Na^+ and Ca^{2+} relations in $meq\,l^{-1}$ determined that a cationic exchange process takes place

in the loessic sediments in the Salado River drainage basin, influencing the chemical characteristics of both groundwater and surface water.

The above results led us to analyse a different environment, Lobos shallow lake in the Salado River drainage basin (35°17′S; 59°07′S) west of Chascomús Lake, and further from the sea. Previous reports on Lobos chemical characteristics mainly referred to salinity and ionic composition (Ringuelet, 1962; Ringuelet et al., 1968; Mariñelarena and Conzonno, 1997). A large concentration of sand size gypsum crystals has been recognized in the clastic sediments filling up Lobos Lake, interspersed, in friable mudstones, assigned to a mixohaline paleoenvironment (Dangavs and Blassi, 1992). Various gypsum occurrences in the Salado River basin have the same characteristics and they are probably related to the presence of sulphate rich groundwaters, which ascended via capillarity action to evaporate in the arid paleoclimatic phases during the Holocene.

Surface and shallow groundwaters from the Lobos lake region were sampled during August 1998. Surface waters TDS mean values were 2922 ppm (1354–5146 ppm) and pH 7.31 (6.65–7.68). Water chemical composition is shown in Fig 4. In spite of Na^+ being the principal cation and cations showing the same relations in $meq\,l^{-1}$ as in the Chascomús region, relations between anions were different as $Cl^- > SO_4^{2-} > HCO_3^-$. Piper's diagram (Fig. 5) shows that 100% of the surface waters were strongly alkaline ($Na + K > 75\,meq\,l^{-1}\%$), 83.3% without dominant anion type (Cl, HCO_3 and SO_4 $< 50\,meq\,l^{-1}\%$) and the remainder of chloride type.

Groundwater TDS mean values were 1495 ppm (965–3360 ppm) and pH 7.31 (6.65–7.68). Fig. 6 shows water chemical composition. Piper's diagram (Fig. 5) shows that 81.8% were strongly alkaline, 18.2% alkaline; 81.8% were bicarbonated ($HCO3 > 50\,meq\,l^{-1}\%$) and the rest of them were without dominant anion type.

A plot of $Ca + Mg—(SO_4 + HCO_3 + CO_3)$ against Na–Cl was performed for surface waters (Lobos shallow lake and tributaries) (Fig. 7). Results indicated a good correlation ($R^2 = 0.97$) and a slope ($p = -1.09$) that tends to the theoretical value of -1 indicating a cationic exchange process between Ca^{2+} and Na^+. As expected, the same plot for shallow groundwaters (Fig. 8) showed slope ($p = -1.01$) and $R^2 = 0.93$ confirming that this process takes place in the Pampean loessic sediments.

The main source of groundwater sulphates is gypsum dissolution, which can be found in loessic sediments as small granular nodules of subcrystalline interior, or as small rosettes formed by the union of small crystals. In these cases, gypsum evolves to groundwater through meteoric filtrations (lixiviation and re-crystallization)
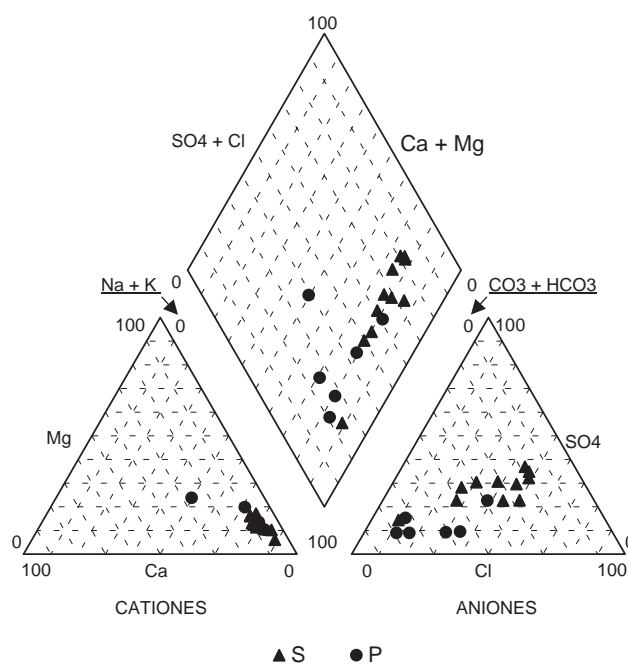

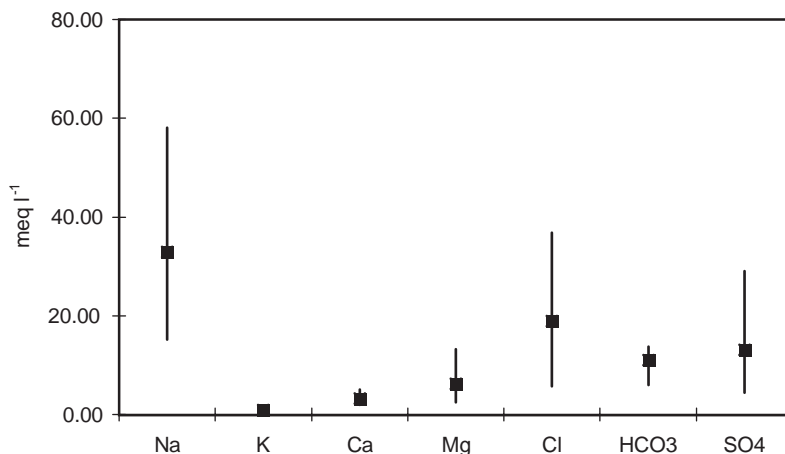Fig. 5. Lobos Piper diagram (S: surface water; P: groundwater).

Fig. 4. Chemical composition of Lobos surface water.

from the superimposed ashes, rich in amorphous and crystalline calcium sulphate (Frenguelli, 1955).

The relation between the shallow groundwater SO_4^{2-} and Ca^{2+} content is $[SO_4^{2-}] = 1.47 [Ca^{2+}]$ ($R^2 = 0.45$), the slope being 50% greater than the value expected for gypsum dissolution. This is due to the fact that Ca^{2+} concentration is controlled not only by gypsum dissolution, but to the calcite precipitation–dissolution equilibrium, the cationic exchange process and the weathering of calcium plagioclases although the latter shows slow reaction kinetics.

If we compare surface and groundwater salinity (TDS: 2922 and 1495 ppm), it is evident that surface water is enriched two-fold by the evaporation process. If we consider chloride as the conservative element, the evaporation factor should be $[Cl^-]_{surf}/[Cl^-]_{groundwater} = 3.5$. The relation for sulphate is 4.9 that for Ca is 1.7, indicating that evaporation alone cannot explain these results. Gypsum dissolution in lake sediments seems to be the other process that determines water chemistry in Lobos shallow lake.

The differences observed for Ca concentration are explained by ionic exchange and calcite precipitation. The occurrence of the first process has been already demonstrated by the use of ionic relations. The saturation indices (SI) were calculated using the
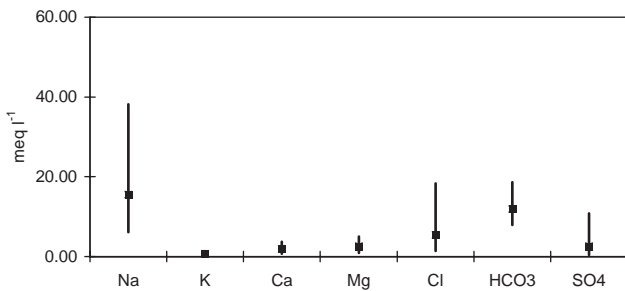
WATEQF (Plummer et al., 1978) program. Subsaturation was observed for gypsum, suggesting that dissolution will take place until the equilibrium concentrations are attained, while oversaturation was observed for calcite, indicating possible precipitation of this mineral phase.

These findings encouraged us to analyse ionic relations for other shallow lakes in the Salado River drainage basin, using our own and literature data. The plot (Fig. 9) of $Ca + Mg - (SO_4 + HCO_3 + CO_3)$ against
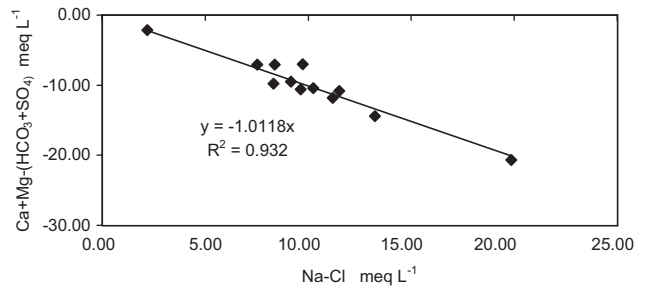

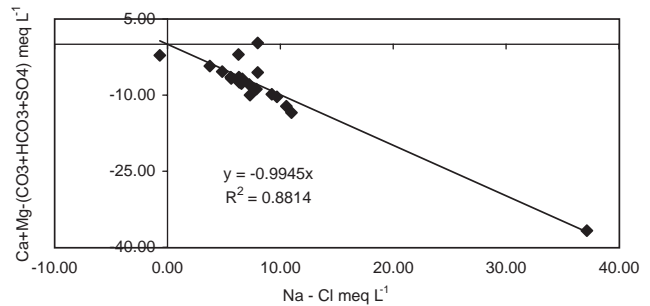Fig. 8. Ionic relations for Lobos groundwaters.

Fig. 9. Ionic relations for shallow lakes in Salado River drainage basin (data from: Dangavs and Dallasalda, 1977, Mariñelarena and Conzonno, 1997; Fazio et al., 1998, Ringuelet et al., 1968; Drago and Quirós, 1996 and Miretzky et al., 2000).

Fig. 6. Chemical composition of Lobos groundwaters.

Fig. 7. Ionic relations for Lobos surface water.

Na–Cl indicate a good correlation ($R^2 = 0.88$). The value of the slope ($p = -0.99$) clearly suggests the cation exchange process between Ca^{2+} and Na^+ for all the shallow lakes under consideration.

5. Conclusions

The principal geochemical processes determining the chemical composition of Pampean shallow lakes were analyzed through ionic relations in the Salado River drainage basin (Buenos Aires, Argentina). The "Encadenadas de Chascomús" system was the first system to be studied. When geochemical processes were analyzed through Gibbs' cationic diagram, deviations were found which could not be explained by dissolution of ancient salts of marine origin since sodium content was larger than chloride content ($meq\,l^{-1}$). This behavior was explained considering a cation exchange reaction between calcium and sodium in the hydrochemical evolution of groundwater through Pampean loessic sediments, with local groundwater one of the sources of surface waters. As expected, no deviations from the Gibbs anionic diagram were observed.

Surface and shallow groundwaters from Lobos lake region were analyzed through ionic relations in order to confirm that the cation exchange process takes place in the Pampean loessic sediments. This environment differs from "Encadenadas de Chascomús" system, since a large concentration of sand size gypsum crystals are present in the clastic sediments of Lobos shallow lake. Dissolution of calcium sulphate promotes the enrichment of surface waters in sulphate in comparison with shallow groundwaters. Nevertheless, calcium content does not show the same increase, as its concentration is controlled not only by gypsum dissolution but also by the cationic exchange process and calcite precipitation.

When ionic relations were considered for other shallow lakes in the Salado River drainage basin, the cationic exchange process was confirmed for all of them. Therefore, the main geochemical processes involved in water chemistry are: weathering of mineral phases-cation exchange and evaporation–crystallization. The plot of $Ca + Mg–(SO_4 + HCO_3 + CO_3)$ against Na–Cl is a simple and precise tool to analyse the cation exchange process, not previously described in this region.

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