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ORIGINAL ARTICLE

Chemical classification of the water in a lowland river basin (Salado River, Buenos Aires, Argentina) affected by hydraulic modifications

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Abstract The main ions were measured seasonally during two years at 13 sampling stations in the Salado River and its main tributaries. The importance of each ion was assessed by standard methods used to examine ionic composition and by multivariate methods. The *K*-means clustering and Principal Component Analysis were applied to the percentages of the major ions. The concentration of the major cations are in the order $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ and the major anions, $Cl^- > SO_4^{2-} > HCO_3^- > CO_3^{2-}$, and the salinity was high (mean TDS 2,691 mg l^{-1}) due to sodium chloride. Using the proportions of the ions was possible to identify seven types of water within the basin related to discharges of different river sub-catchments and from endorheic catchments (in a sand dune region) actually connected with the basin by canals. The chemical composition of the basin is consequence of surface waters receiving salts from groundwater, evaporation and weathering of Post-Pampeano materials, and of anthropogenic impact by diversion between subcatchments for flood control. These results allowed us to test the marked effects on the ionic balance of basin at the base of a diversion management from endorheic catchments characterized by high salinity waters.

Keywords Saline lowland river · Water quality · Endorheic catchment diversion · Multivariate analysis

Introduction

The majority of rivers in the world have total dissolved solids (TDS) of less than 500 mg/l but others with the highest values are either a product of pollution (the most representative European rivers) or due to their location in arid and semiarid regions (Gaillardet et al. 1999). When the salinity differs by two or three orders of magnitude from the most common natural concentrations they can be considered extreme natural rivers. Those rivers characterized by highly mineralised water are known as ‘‘salted rivers’’ resulting from the weathering of evaporitic sediments (gypsum, halite). These ‘‘evaporated rivers’’ have a marked variation with time and the water type that dominates contains NaCl related to redissolution of recently precipitated evaporates during floods. Such evaporated rivers occur mainly in endorheic and arheic regions (Meybeck 1996).

Lithology and the hydrological regimens of rivers are major regulators of their chemical composition and, are related to the pattern of discharge (Meybeck 1996). The monitoring of sub-catchments is very important because this information provides simple relationships between the ionic concentrations of the river water, soil water and groundwater inputs, which is useful for understanding the water characteristics at all basin scales (Smart et al. 1998).

The use of binary and ternary diagrams is frequent for characterization of water types and their origin but several have limitations for some types of water (Gibbs 1970; Kilham 1990; Baca and Threlkeld 2000). More recently, multivariate analysis offers more accurate results for the description of water types (Mc Neil et al. 2005). Multivariate analysis provides a useful tool with which to interpret a complex data set and has been widely applied to ecological studies in rivers (Perona et al. 1999).

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In recent decades, a notable increase of surface and groundwater salinization has been detected in semiarid regions of the world and this situation is becoming a critical issue for water resource management (Herczeg et al. 2001). For this reason, and in order to improve the management and protection of these water resources, it is necessary to know the sources of the salts and their transport mechanisms. In areas with low relief and high rates of evaporation, it is possible that atmospherically derived salts have reached very high concentrations in soil water that eventually recharges the aquifer. The forms of salinization in the Salado River basin are manifested in the saline river and streams and superficial efflorescence in shallow waters of the watershed. The mobilization of large amounts of stored salts in the groundwater of endorheic areas through artificial diversion (channels) with an alteration of the hydrological balance is a cause of the problem. Knowledge of the dynamics and the sources of salts can be useful for reasonable management of these hydrological resources. Results from investigations carried out in the lower basin and drained channels indicate that the water type in this river sector is dominated by NaCl and the TDS values are related to high and low water periods (Conzonno et al. 2001).

The main objectives of this paper are to answer the following questions: (1) What are the ionic characteristics of the water in the Salado basin? (2) What is the effect of water diversion from endorheic areas as sources of solutes to the main channel? (3) What is the effect of tributaries on the ionic composition of the water in the river?

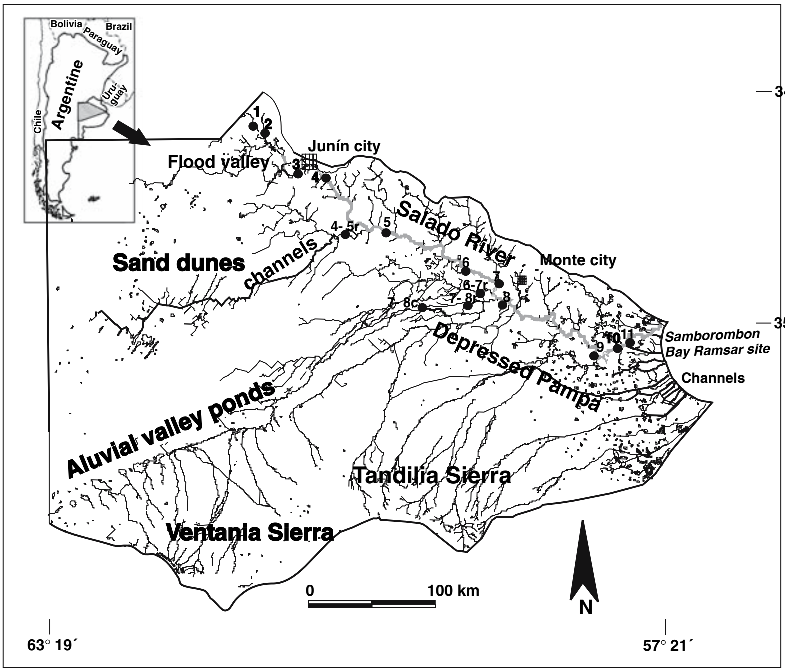
Study area

The Salado River is a typical lowland river with a watershed of approximately 150,000 km^2 (including the endorheic areas related to the canals), length of approximately 600 km and a low slope (mean 0.107 m/km). Different zones can be distinguished within the basin, which reflect geological, soil and agricultural influences and ecological characteristics, and have different parameters, such as sulphate and chloride concentrations/flow relationships, which have been described in detail by Gabellone et al. (2003, 2005) (Fig. 1).

Historical information confirms that the river had a non-perennial regime in dry periods during the nineteenth century and the beginning of the twentieth century (Moncaut 2003). Since approximately 1960, the basin has suffered a humid period (Fig. 2).

The geological information of the Buenos Aires province is fragmentary and dependent on local studies. The basin of the Salado River is underlain at depth by Pre-cambrian basement igneous and metamorphic rocks, which in turn are variously overlain by Pre-Paraná sediments including Olivos, Las Chilcas and General Belgrano Formations. Some of paleozoic sediments are exposed in the southern mountains. The Paraná Formation (El Verde) clays are present throughout the catchment except in the Laprida embayment between the Ventana and Tandil mountains, and along the flanks of those mountains. Overlying the Parana Formation in the northeast are the sands of the Puelche Formation. These are medium to fine-

Fig. 1 Main drainage system and locations of sampling stations in the Salado River basin



grained, friable quartzose sands (Aradas et al. 2002). The Pampeano extends throughout the catchment in the south. The basal few metres of the Pampeano unit are argillaceous with the bulk of the unit consisting of clayey and sandy silts (loess) with caliche (calcium carbonate soil horizons). The most significant deposits occur within the interfluve between the Rio Salado and the Saladillo - Vallimanca streams as important sand dunes (Malagnino 1988) (Fig. 3; Table 1).

The Pampeano Formation forms the top of the aquifer regionally. Locally, sand dunes add to the system thickness. All of the units are in hydraulic continuity, and the system may be considered regionally unconfined, with a free water surface at the upper boundary, although variably distributed confinement and semi-confinement do occur (Kruse and Zimmermann 2002).

The groundwater located in the Salado River basin contains NaCl with a salinity that reached 20 g/l due to the low flow velocity that facilitates salt incorporation and the incidence of marine ingressions that occurred during the Holocene. Some groundwater flow occurs to the Rio Salado and to the Vallimanca and Saladillo streams. Groundwater with a TDS of 1,000 mg/l is located at the southern sector of the basin, near to Tandil and the Ventana mountains and between Junin and San Miguel del Monte cities (Auge et al. 2002). The presence of sulphate in groundwater could be related to the intra-sedimentary gypsum deposits (upper Pleistocene) (Dangavs and Blassi 2002).

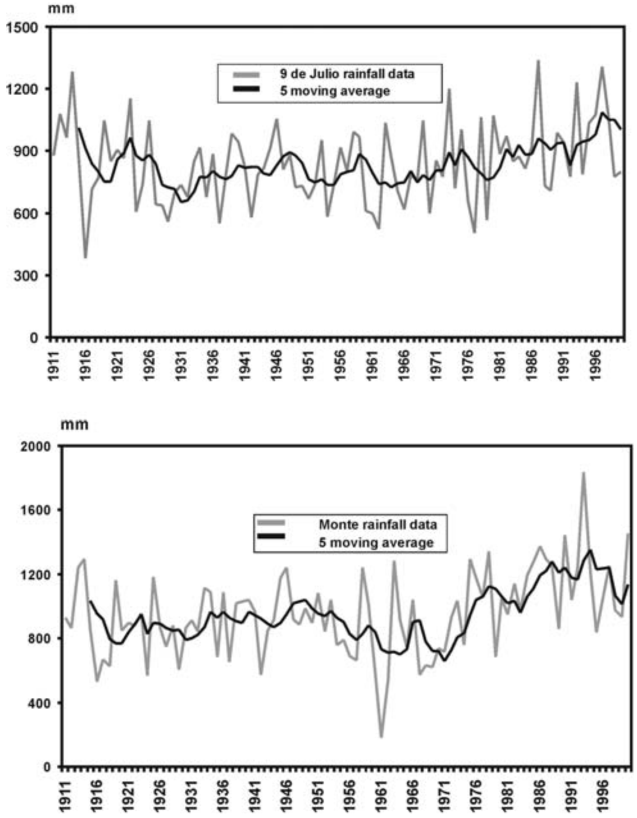


Fig. 2 Historical rainfall records and five moving averages of selected sites within the Salado River basin (9 de Julio city located in headwaters and San Miguel del Monte town in the middle river sector)

In the west, an internal groundwater basin was historically present, but has been breached by the construction of the canal Jauretche-Mercante-Italia in the late 1980s that discharges into the Salado River through the Saladillo stream. Surface waters received salts from the groundwater, evaporation and weathering of Post-Pampeanos materials, runoff and diversion between sub-catchments (Plan Maestro 1999).

The presence of wetlands and lakes, progressively more common from west to east, and dictated by the low relief and very thin unsaturated zone, indicates that the groundwater regime is severely constrained by the surface water regime. This shows that a conventional surface water drainage system is not relevant except in southern mountain areas. The water table is directly subject to evapotranspiration, which is a significant control on heads. The regional flow is relatively small, which is consistent with the relatively small hydraulic conductivity, the very gentle regional gradient and the relatively high groundwater salinity (Aradas et al. 2002).

Materials and methods

In the northern sector of the basin five sampling stations were established: Station 1 (St 1) Salado stream; Station 2 (St 2) Piñeiro stream; Station 3 (St 3) Junín 1; Station 4 (St 4) Junín 2; Station 4–5r (St 4–5r)–Saladillo stream that

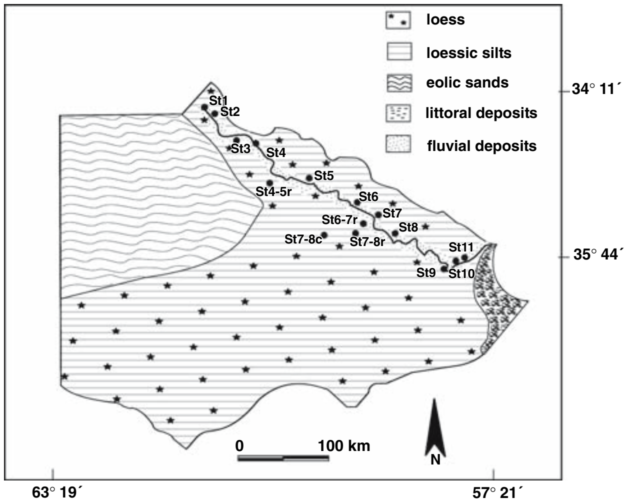


Fig. 3 Geological features of the Salado River basin according to Fidalgo (1999)

Table 1 Stratigraphic scheme of the Salado River basin (modified from Yrigoyen 1975)

Formation	Epoch	Lithology
Médano Invasor or Junín (Postpampeano sediments)	Holocene	Fine sand to silty sand
Pampeano	Pleistocene	Loess
Puelche	Plio-Pleistocene	Fine to medium sands with clay matrix
Paraná	Late Miocene	Clays, clayey and carbonate sands and marine fossils
Olivos	Early Miocene	Sandstone, clay with gypsum and evaporites
Las Chilcas	Paleocene	Siltstones and marine clays
General Belgrano	Cretaceous	Consolidated sandstones and sandy siltstones
	Paleozoic	Quartz and limestones
Basement igneous and metamorphic rocks	Precambric	Granites and gneiss

receives the Jauretche–Mercante República de Italia canals; Station 5 (St 5) Achupallas. In the Middle West sector of the basin three sampling stations were established: Station 6 (St 6) Ruta 30; Station 6–7r (St 6–7r). Saladillo–Vallimanca stream (a sub-basin), one of the main tributaries of the Salado River, which originates in the Ventania Mountains and Station 7 (St 7) Roque Pérez. In the zone named ''depressed pampa'' seven sampling stations were established: Station 7–8r (St 7–8r) Las Flores stream (sub basin) that has its source in the Tandilia Mountains; Station 7–8c (St 7–8c) Canal 16 that regulates the discharge of Vallimanca stream; Station 8 (St 8) Gorchs left bank, Station 8r (St 8r) Gorchs right bank; Station 9 (St 9) General Belgrano; Station 10 (St 10) El Destino and Station 11 (St 11)–La Postrera located at 84 km from the mouth of the Salado River.

No sampling stations were established downstream of Station 11 because, below here, 80% of the river discharge runs through two canals starting at 69 km from the river mouth.

The sites were visited initially in March 1997, and then quarterly on a seasonal basis through to the autumn of 1999. On the first four occasions, 14 sampling stations were sampled. During the period May 1998–June 1999, two further tributaries were also included because they bring in water from peri-mountain sub-basins (stations 7–8c and 7–8r) (Fig. 1). The incorporation of these sites improves the interpretation of the results.

At each visit, the water samples were collected in 1 L acid-cleaned polyethylene bottles, transported back to the laboratory in an ice-cooled isolation box and stored in the dark at 5–8 °C prior to the analysis.

Chloride was determined according to the method 4500-Cl B recommended by APHA (1995), sulphates by the turbidimetric method described by Tabatabai (1974). The sodium and potassium concentrations were obtained by flame photometry (methods 3 500 Na D and 3500 K D respectively, recommended by APHA (1995)). Calcium concentration was determined by the EDTA titrimetric method (3500 Ca D in APHA 1995) and Magnesium by calculation (3500 Mg E in APHA 1995). Total Alkalinity was determined by titration (method 2320 B in APHA 1995). The concentrations of carbonates and bicarbonates were estimated based on stoichiometric relationships. Total dissolved salts was calculated as the sum of the major cations and anions. The balance of ions for Piper diagrams was generated with the major anions and cations.

Data on discharge are scarce both in terms of frequency and location. There are only four gauges with a few available data taken from Dirección de Hidráulica of Buenos Aires province.

The water types were distinguished taking in account those ions that contribute more than 10% to the TDS. The K-means clustering technique (Güller et al. 2002, Mc Neil et al. 2005) was used to divide each group into the seven water types of the Salado basin. Multivariate analysis was performed using percent equivalent of the major ions corresponding to all sites on each sampling occasion and the mean value of each site. Principal Components Analysis (PCA) was carried out from a correlation matrix and for the best graphic representation of the cases the axes were rescaled using standard deviation multiplication (Ter Braak 1995).

Results

The waters of the Salado River and its tributaries are alkaline, with a mean pH of 8.63 (7.6–9.7) and mean TDS values reached 2 691 mg/l (912–5 594).

The concentrations of the major cations are generally in the order of $Na^+ > Mg^{2+} > Ca^{2+} > K^+$. The major anion concentrations follow the same trend in all basins, namely $Cl^- > SO_4^{2-} > HCO_3^- > CO_3^{2-}$ (Fig. 4; Table 2).

The main cation in the basin is Na^+, with a similar concentration at all sampling stations located in the main river course but with differences in the tributaries (Fig. 4). Mean values of Na^+ were recorded in tributaries, and also

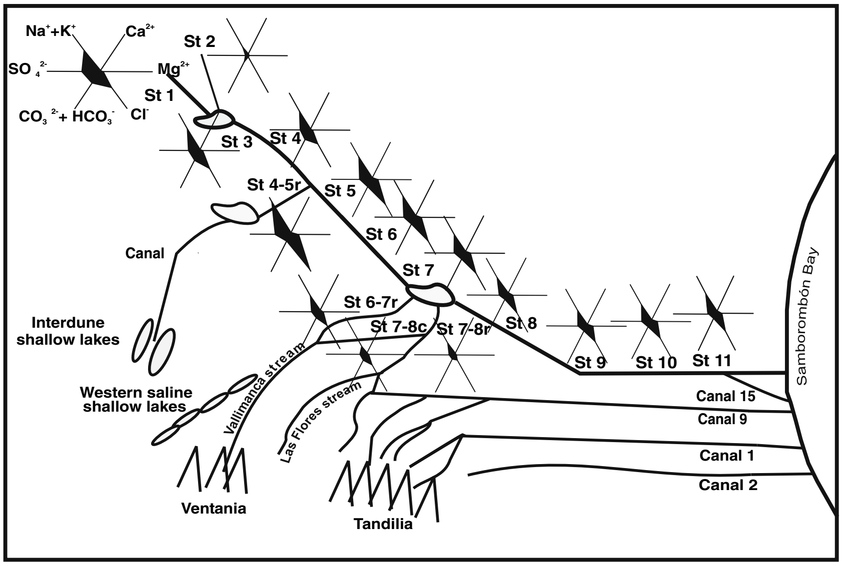


Fig. 4 Mean ionic composition (meq/l) of the sampling stations located at the Salado River basin expressed by radial plots

the highest (Saladillo stream 43.5 meq/l) and the minimum (11 meq/l) in Piñeiro and Las Flores streams (Table 2). As a percentage, this cation always represents more than 25 % of the total ions. Magnesium is the second most important cation with concentrations lower than those of Na^+: The water of the Saladillo stream is the main source of Mg^{2+} to the river (mean 10 meq/l), and influences the downstream sampling stations, including those located in the lower sector of the river (Fig. 4). All of these sites showed similar concentrations of this cation (7.5 meq/l). Lower concentrations (3 - 4 meq/l) of Mg^{2+} were recorded in the headwaters and tributaries of the middle sector (Table 2). Calcium ion exhibited the same trend in the headwaters as Mg^{2+} (1.6 meq/l), and maintained similar values (approximately 3 meq/l) (Fig. 5) in the rest of the basin. Potassium showed lower concentrations relative to the other main cations in the basin (0.3–1 meq/l), with lower values in the lower sectors of the main course and tributaries that discharge above this sector.

Among the main anions, CO_3^{2-} presented the lowest mean concentrations, with its maximum in the headwaters and the main tributary of this sector (Salado stream). The mean values of 3 meq/l coincided with pH greater than 8.8. Chloride is thus the main anion in this basin (Fig. 4). The maximum concentrations (47 meq/l) were recorded in Saladillo stream, generating the increase in the middle sector of the river (mean value 31 meq/l). The incorporation of water from other basin sectors, which have, mean values of chloride about 6–18 meq/l produced a decline in the importance of this anion in the lower sector (23 meq/l). HCO_3^- and SO_4^{2-} have the same importance in the basin but with a different behaviour. The concentration of HCO_3^- was similar throughout the basin (mean 8 meq/l), with a slight decrease in the sector nearest to the mouth (mean 6.7 meq/l) due to the incorporation of tributaries with minor ion concentrations (mean 5–7 meq/l). The SO_4^{2-} showed the same trend as the chloride, with a considerable influence of two tributaries (Salado mean 17 meq/l and Saladillo stream mean 18 meq/l) in the headwaters. The other tributaries showed a mean value of 8.6 meq/l. The Piñeiro stream (the tributary with the lowest discharge) presented the lowest sulphate (mean 2.1 meq/l) and chloride concentrations (mean 1.8 meq/l). For this reason this stream is clearly isolated from the rest of the sampling stations in the Piper diagram (Fig. 5).

According to the Piper diagram, the water is sodium chloride and sulphate dominated at all the sampling stations except at Piñeiro stream where the water is sodium bicarbonate dominated (Fig. 5). Canal 16 and the Piñeiro and Las Flores streams are the least mineralized whereas the Salado and Saladillo stream showed the highest concentrations of solutes (Table 2).

It was possible to distinguish seven different types of water within the basin based on the ions that contribute more than 10% to the total. One group is formed by the sampling stations located in the headwaters of the Salado River, characterized by moderate conductivity values and sodium chlorinated, sulphated, and bicarbonated waters (water type 1). The stations located in the middle sector of the river, that receives the discharge of the Saladillo stream (water type 2), are characterized by the highest conductivity values and sodium chloride and sulphate dominated waters (water type 3). This tributary presented the same ionic composition but with the highest mean conductivities. After the confluence of tributaries from mountain regions (water type 7) (subcatchments), the sampling stations located in the lower river sector are charaterized by con-

Table 2 Average values and ranges (meq/l) of water chemistry at sampling locations in the main course of the Salado River and tributaries (*n*: number of samples, SD: standard deviation)

	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}
St 1 (n = 6)								
Mean (SD)	4.04 (2.9)	11.45 (2.57)	22.11 (10.60)	17.07 (8.22)	27.89 (8.43)	0.96 (0.52)	1.14 (0.52)	3.31 (1.15)
Range	1.19–7.92	8.00–14.60	13.47–42.90	9.70–28.83	12.34–37.76	0.43–1.78	0.74–2.16	1.80–5.00
St 2 (n = 3)								
Mean (SD)	0.24 (0.15)	7.25 (0.83)	1.80 (0.28)	2.09 (0.26)	10.99 (1.28)	0.6 (0.08)	3.01 (1.52)	2.51 (0.79)
Range	0.09–0.396	6.40–8.05	1.60–2.13	1.80–2.25	9.53–11.95	0.53–0.68	1.76–4.70	1.80–3.36
St 3 (n = 6)								
Mean (SD)	2.99 (2.96)	10.41 (2.07)	24.40 (9.28)	13.75 (3.79)	28.50 (5.63)	1.23 (0.48)	1.70 (0.46)	4.15 (1.44)
Range	0.06–8.38	7.20–13.05	16.66–37.66	9.68–19.37	20.10–36.37	0.68–2.00	1.18–2.35	2.38–5.99
St 4 (n = 6)								
Mean (SD)	2.00 (1.61)	10.97 (2.39)	18.99 (6.78)	11.73 (4.63)	24.32 (6.56)	0.86 (0.48)	1.54 (0.50)	3.50 (1.71)
Range	0.71–4.95	9.50–15.51	10.30–30.72	5.71–19.37	19.26–33.70	0.3–1.67	0.78–2.16	1.80–6.40
St 4–5 (n = 6)								
Mean (SD)	0.70 (0.57)	8.70 (1.40)	47.86 (11.33)	18.24 (3.90)	43.52 (14.84)	0.99 (0.49)	2.81 (0.66)	10.47 (2.19)
Range	0.20–1.78	7.10–10.80	31.30–63.45	14.15–24.07	28.60–63.34	0.25–1.55	1.96–3.92	7.79–13.53
St 5 (n = 6)								
Mean (SD)	0.56 (0.44)	9.62 (2.34)	33.63 (10.38)	14.87 (4.18)	29.25 (5.87)	0.86(0.50)	3.14 (0.89)	8.12 (3.46)
Range	0.20–1.39	7.50–13.81	20.48–49.08	10.67–20.09	20.81–36.29	0.15–1.55	2.16–4.70	4.43–12.96
St 6 (n = 6)								
Mean (SD)	0.44 (0.25)	8.67 (3.69)	32.09 (16.02)	14.34 (6.74)	27.74 (4.25)	0.93 (0.34)	2.81 (0.81)	7.41 (3.57)
Range	0.14–0.79	4.11–15.31	19.43–61.6	5.49–24.55	23.18–33.24	0.45–1.35	1.96–3.72	4.02–13.78
St 7 (n = 6)								
Mean (SD)	0.41 (0.24)	8.09 (3.35)	27.19 (10.53)	13.36 (6.13)	24.38 (5.87)	0.65 (0.36)	3.04 (1.36)	7.11 (4.53)
Range	0.20–0.79	5.50–14.51	16.62–45.58	4.60–21.58	19.09–32.47	0.28–1.23	1.96–5.68	3.20–15.91
St 6–7r (n = 6)								
Mean (SD)	0.50 (0.40)	7.48 (2.34)	18.01 (8.23)	9.71 (4.79)	21.00 (7.99)	0.61 (0.31)	2.94 (0.98)	4.74 (1.45)
Range	0.06–0.99	4.60–11.10	8.32–30.91	4.73–17.62	6.14–27.48	0.04–0.90	1.57–4.51	2.38–6.56
St 8 (n = 3)								
Mean (SD)	0.36 (0.30)	5.61 (1.30)	24.28 (15.99)	9.73 (5.98)	22.88 (10.78)	1.08 (0.34)	3.20 (0.60)	7.38 (5.22)
Range	0.02–0.59	4.70–7.10	9.66–41.36	6.07–16.62	12.38–33.93	0.88–1.48	2.55–3.72	3.77–13.37
St 7–8r (n = 4)								
Mean (SD)	0.09 (0.07)	5.33 (0.98)	6.69 (2.82)	6.27 (1.37)	11.096 (5.26)	0.38 (0.39)	2.50 (0.25)	1.99 (1.48)
Range	0.04–0.198	4.30–6.60	4.17–10.70	4.73–7.94	6.84–18.32	0.07–0.95	2.16–2.74	0.98–4.18
St 7–8c (n = 4)								
Mean (SD)	0.33 (0.35)	7.18 (2.77)	14.48 (10.66)	8.50 (3.189	14.19 (5.31)	0.40 (0.26)	2.99 (0.70)	3.47 (3.46)
Range	0.06–0.79	4.30–9.60	6.55–29.34	4.23–11.17	7.03–19.14	0.04–0.65	2.35–3.92	0.20–7.95
St 9 (n = 6)								
Mean (SD)	0.19 (0.14)	6.31 (2.06)	20.92 (10.64)	10.49 (5.70)	20.35 (9.03)	0.56 (0.33)	2.61 (0.64)	7.48 (3.07)
Range	0.02–0.44	2.60–8.70	5.99–33.30	4.33–17.61	10.32–33.24	0.26–1.05	1.96–3.72	4.02–11.73
St 10 (n = 6)								
Mean (SD)	0.18 (0.13)	6.92 (1.76)	22.60 (12.87)	11.19 (5.59)	21.76 (5.90)	0.68 (0.27)	2.94 (0.97)	7.60 (3.33)
Range	0.04–0.38	4.20–9.40	6.18–37.86	6.48–19.11	11.05–26.66	0.36–1.00	1.76–4.12	3.20–11.56
St 11 (n = 6)								
Mean (SD)	0.35 (0.43)	6.87 (2.40)	25.43 (14.51)	11.32 (5.84)	26.49 (13.42)	0.75 (0.37)	3.56 (0.60)	7.54 (3.66)
Range	0.04–1.19	3.60–10.40	11.59–50.55	6.31–21.08	11.46–50.44	0.32–1.35	2.94–4.70	1.97–10,99

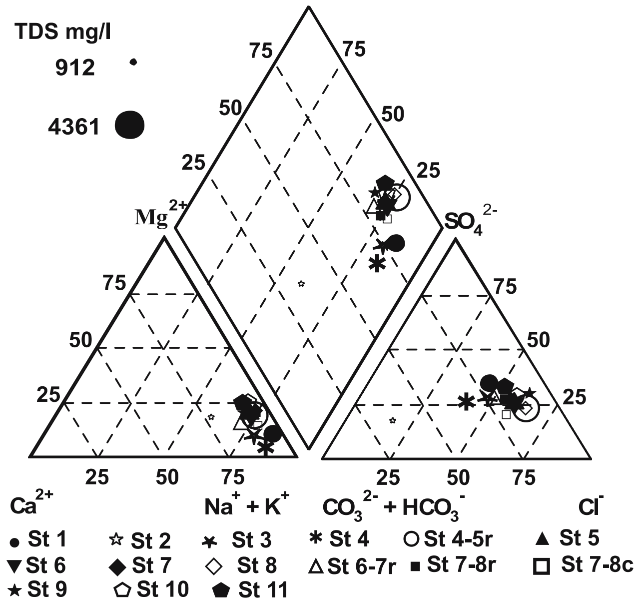


Fig. 5 Piper diagram of the main ions (meq/l) of the sampling stations located in the Salado River basin

ductivity values less than those of the middle sectors and dominated by sodium and magnesium chloride and sulphate (water type 5). The Saladillo–Vallimanca stream (water type 4) has a water type considered transitional, with moderate conductivity and sodium chloride, sulphate, and bicarbonate waters. The tributaries characterized by low conductivities are grouped in two types of water: one group is formed by a small stream located at the headwaters (water type 6), and the other by tributaries originating in mountain regions (water type 7) (Table 3).

The lowest values of Ca^{2+}/Na^+ and HCO_3^-/Na^+ ratios were obtained in the headwaters (sites 1, 3 and 4) and Saladillo stream (4–5r) and the highest values correspond to the tributaries originating in the mountain regions and Piñeiro stream (Fig. 6).

In samples obtained on both riverbanks, downstream of the confluence between head and sub catchments waters, marked differences in solute concentrations were recorded. On the left bank, chloride was the main ion.

At a sector nearest station 8, sampling was done from both banks because in this location the Salado River receives, simultaneously, the discharges of Saladillo–Vallimanca stream, Canal 16 and Las Flores stream. It was possible to detect a noticeable difference in water composition because on the left bank there was a marked dominance of chloride in respect to the other anions that differed from the ionic proportion on the right bank where the tributaries discharge. The proportion of sodium was similar on both banks but the absolute values were highest at the bank with water incorporated from the river (Fig. 7).

PCA analysis and *K*-means clustering

The analysis of all sampling occasions, covering the different water types identified in the basin, explained 54.94 % of the total variance in the first two axes. All samples from the Piñeiro stream (water type 6) related to the bicarbonate concentration and least mineralised waters, are located in the positive sector of factor 1. All samples from the Saladillo stream (water type 2), and the majority of samples from the middle and lower river sectors, with chloride and sulphate waters, are situated in the negative sector. All samples from the headwaters are positioned in the positive sector of factor 2 (water type 1) whereas the negative sector contained all samples from tributaries with low mineralization, as well as the Saladillo stream, and the majority of samples obtained in the middle and lower river sectors. Mg^{2+} determines this factor in the negative sector and carbonate in the positive ones (Fig. 8; Table 4).

In this figure it can be seen that mainly water types 3 and 5 (middle and lower river sectors) are located in the positive sector as well as in the negative ones of factor 1. This pattern would be related to the hydrological condition at the time the samples were taken. Those placed in the negative sector represent low water conditions (October 1997: 87 m^3/s estimated for St 10, and February 1999: 35 m^3/s estimated for St 10) with a major ionic component of chloride, whereas those in the positive sector represented samples from high water periods (May 1998: 481 m^3/s estimated for St 10 and October 1998: 230 m^3/s estimated for St 10) with an increase in the relative importance of the bicarbonate ion.

In order to compare the seven types of water determined by their dominant ions, the *K*-means method was applied, predetermining seven clusters (Fig. 9). Cluster 1 is formed only by the Piñeiro stream, which is characterized by low solute concentrations, bicarbonates as the major anion, and the highest concentration of calcium. Cluster 2 includes Saladillo Vallimanca stream and Canal 16 because both have intermediate chemical compositions with respect to all the other sites sampled. Cluster 3 is formed of headwater sites due to the relative contribution of carbonates. Las Flores stream formed cluster 4 because this tributary has low salinity but smaller relative proportions of carbonates and bicarbonates than Piñeiro stream. Cluster 5 is formed by the middle sectors of the river with influence from the upstream tributary (Saladillo stream), and contained more chloride than sodium. Cluster 6 is formed by the sites near to the river mouth and contained more magnesium (as a percentage) than the other clusters. The last cluster is formed only by the Saladillo stream and is dominated by chloride (Fig. 9).

Similar results were obtained with both methods of analysis for the entire basin with the exception of Canal 16.

Table 3 Main = characteristics of the seven types of water of Salado River basin

Water types	Sites	Major cations (meq/l)	Major anions (meq/l)	Conductivity (µS/cm)	Description
1	Salado stream	Na^+	Cl^- SO_4^{2-} HCO_3^-	5,514 (2,430–11,200)	Moderate conductivity with HCO^{3-}, $SO4^{2-}$
	Junin 1	Na^+ Ca^{2+}	Cl^- SO_4^{2-}	4,719 (2,890–7,190)	
	Junin 2	Na^+	Cl^- SO_4^{2-} HCO_3^-	3,667 (2,300–5,940)	
2	Saladillo stream	Na^+	Cl^- SO_4^{2-}	6,389 (3,650–7,820)	High mean conductivity moderate conductivity
	Achupallas	Na^+	Cl^- SO_4^{2-}	6,005 (2,740–9,800)	
3	Ruta 30	Na^+	Cl^- SO_4^{2-}	5,380 (2,790–9,600)	With high maximum values
	Roque Pérez	Na^+	Cl^- SO_4^{2-}	5,245 (2,550–8,360)	
4	Saladillo-Vallimanca stream	Na^+	Cl^- SO_4^{2-} HCO_3^-	3,099 (1,500–5,590)	Moderate conductivity moderate conductivity with low minimum values
	Gorchs	Na^+ Mg^{2+}	Cl^- SO_4^{2-}	4,524 (1,030–7,630)	
	Belgrano	Na^+ Mg^{2+}	Cl^- SO_4^{2-}	3,573 (930–5,910)	
5	El Destino	Na^+ Mg^{2+}	Cl^- SO_4^{2-}	3,732 (1,130–6,260)	
	La Postrera	Na^+ Mg^{2+}	Cl^- SO_4^{2-}	3,999 (1,370–7,900)	
6	Piñeiro stream	Na^+ Ca^{2+}	HCO_3^-	911 (732–1,130)	Low conductivity with Ca^{2+}
7	Las Flores stream	Na^+	Cl^- SO_4^{2-} HCO_3^-	1,455 (770–2,350)	Low conductivity without Ca^{2+}
	Canal 16	Na^+	Cl^- SO_4^{2-} HCO_3^-	2,495 (1,600–4,690)	

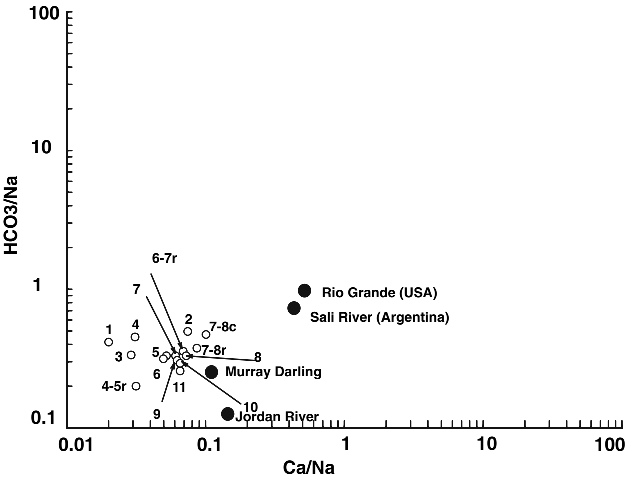


Fig. 6 Diagram of Na ratios of sampling stations in the Salado River basin in South America compared with other saline rivers

This sampling station formed a group with Saladillo Vallimanca in the *K*-means method whereas it is coupled with Las Flores stream using the proportional method (water type 7). It must be considered that this canal regulates the discharge of Vallimanca stream.

Discussion

It is not possible to compare the ionic composition of the Salado River basin with those described for the majority of rivers in the world, which are characterized by a TDS less than 500 mg/l. The values recorded in the Salado were similar to those documented for important polluted European rivers (Rhine, Odra, Weser, Wisla y Don among others), and others located in arid zones such as the Panuco River (México) and the Murray River (Australia). All these rivers have sodium chloride dominated waters, except the Panuco River with its calcium sulphate/bicarbonate water type (Gaillardet et al. 1999).

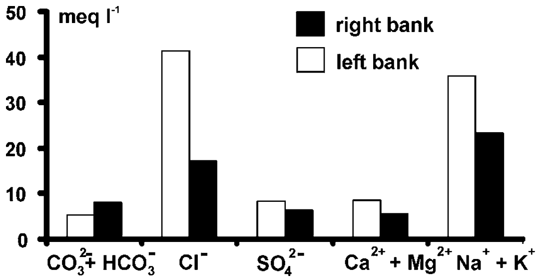


Fig. 7 Ionic composition compared between both banks of the Salado River at the confluence with mountain tributaries, in October 1997

Comparison of the mixing diagram constructed by Gaillardet et al. (1999) with our results from the Salado River basin revealed that all our sampling stations are located near to those from the Murray River (Fig. 6), which is the main example among the 60 analysed rivers of water draining evaporites. The ratios of HCO_3^-/Na^+ of saline rivers such the Sali River in Argentina (Galindo et al. 2001) and Rio Grande in USA (USGS 2007) were similar, but their ratios of Ca^{2+}/Na^+ are higher than those of Salado River basin. The riverine salts of the Rio Grande Basin are derived from leaching of evaporitic rocks (Farber et al.

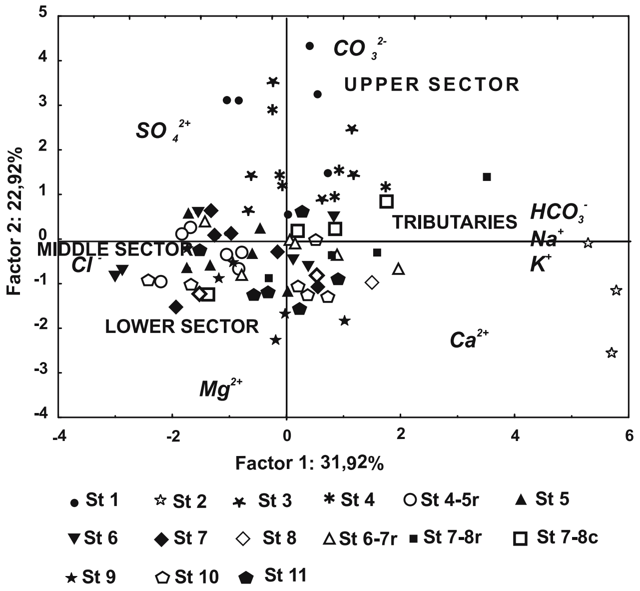


Fig. 8 Factors 1 and 2 of Principal components analysis (PCA) based on the percentages of the major ions for all the samples with spatial identification along the longitudinal axis of the river. Principal variables (ions) at each component and the sampling stations are indicated

Table 4 Factor loadings of each parameters of the PCA analysis

	Factor 1	Factor 2
CO_3^{2-}	0.06	0.82
HCO_3^-	0.66	0.08
SO_4^{2-}	–0.39	0.44
Cl^-	–0.91	–0.11
Na^+	0.57	0.19
K^+	0.64	0.05
Ca^{2+}	0.62	–0.49
Mg^{2+}	–0.16	–0.81

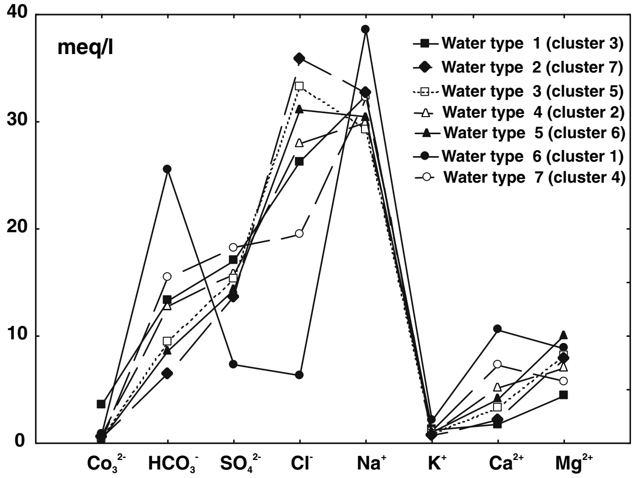


Fig. 9 K-means cluster analysis for seven predetermined clusters (water types) with the mean value of the major ions obtained for each site

2004), and the salts of the Sali River from dissolution of halite and gypsum, and from the weathering of silicates (García et al. 2001). Comparison with a river located in an arid zone (River Jordan) revealed a similar ratio of Ca^{2+}/Na^+ but a smaller HCO_3^-/Na^+ ratio than the Salado River basin. The sources of salts that flow to the River Jordan are geogenic but the magnitude of groundwater discharge depends on irrigation practices in the Jordan Valley (Farber et al. 2004).

Considering the classification proposed by Meybeck (1996) for rivers with high salinity values, the Salado River could be considered as an evaporated river only in those headwaters associated with the mobilization of large amounts of salts stored in the groundwater of endorheic areas through artificial diversion (channels). The rest of the basin is a salted river because the salinity results from the weathering of evaporitic sediments located in quaternary deposits that have suffered desert and humid climatic facies (Iriondo 1999), with the development of continental evaporates and intra-sedimentary gypsum deposits (upper Pleistocene) (Dangavs and Blasi 2002). The salinity decreases significantly in the middle and lower stretches of the river during flood periods (Gabellone et al. 2005).

The type 1 water is restricted to the headwater sector (St 3 and St 4) and included as an order one tributary (St 1) that discharges into the Mar Chiquita lake (flood valley) and from this location begins the main river channel that interconnects two flushing lakes (Gómez and Carpincho). These water bodies are shallow and the area they occupy is more than 150 km^2. All of them presented high salinity readings (more than 8,000 μS/cm during high water periods) and TDS values of 1,0636 mg/l were recorded in summer as a result of evaporation (Ringuelet et al. 1967). In this sector, the mean river flow is less than 30 m^3/s. The type 2 water is represented by Saladillo stream (St 4–5r), with its source in an endorheic area (sand dune region) that is artificially connected with the Salado River basin by means of canals. This water type represents surface waters that receive salts from groundwater, evaporation and weathering of Post-Pampeanos materials, plus runoff and diversion between sub-catchments (Plan Maestro 1999). The Saladillo stream has more influence over the middle sector of the river (water type 3). The transitional water type (4) represents the Saladillo-Vallimanca stream (St 6–7r), with ground- and surface waters that come from a mountain region (Ventania). The increasing presence from west to east of wetlands and shallow lakes dictated by the low relief and very thin unsaturated zone, indicates that the groundwater regime is severely constrained by the surface water regime (Aradas et al. 2002). This water type joins the river with other surface water from another mountain system (Tandilia) (Las Flores stream sub-catchment) characterised by sodium bicarbonate (water type 7) and low TDS values (150–740 mg/l) (Hernández et al. 2002). The major importance of the sodium bicarbonate in the ionic composition of the water types 4 and 7 could be related to the presence of caliche in the pampean sediments of mountain systems (Ventania and Tandilia). The water characteristics of the lower river sector (water type 5) are a result of the discharge from the endorheic sector (sand dune region) linked with those from the Saladillo-Vallimanca and Las Flores sub-catchments. The water type 6 corresponds to an order one tributary (Piñeiro stream) with minor mineralization of the basin but without influence due to its low flow.

We considered, in agreement with Smart et al. (1998), that for a good knowledge of the regional hydrochemical characterization of the Salado River basin it is necessary to include the main natural and artificial tributaries that represent subcachtments in order to identify the source, nature and importance of these areas within the whole basin.

The use of multivariate analysis (Perona et al. 1999; Mc Neil et al. 2005) allowed us to interpret the complex Salado River data. By means of *K*-means cluster analysis it was possible to classify the types of water in a similar way to the usual methods for ionic composition but with the advantage of the synthetic graphical result also obtained. This analysis, combined with PCA performed with all samples, and considering the different water types, permitted their spatial identification along the longitudinal axis of the river represented by the factor 2 and defined by the carbonate concentration in the positive sector and the cation Mg^{2+} in the negative sector. Moreover, differences among samples of each water type were observed, with separation according to the hydrological condition of the river. Changes in solute concentrations, mainly chloride, were detected during low water periods as well as in high water periods.

The use of graphic methods was inadequate to distinguish different types of water in the Salado River basin, because all the sites, except the Piñeiro stream, were included in a group dominated by sodium chloride. The combination of the two approaches we have used (Güller et al. 2002) (proportion of major ions and *K*-means method) gave similar results for an efficient classification of water in the basin and minimized the limitations of either approach.

These results allowed us to test the marked effects on the ionic balance of the Salado River basin of the diversion management from endorheic catchments characterized by high salinity waters. During flooding periods, the discharge of this area throughout the catchment of the Saladillo stream is clearly most important, showing a trend towards secondary salinization in the entire basin. Future modifications of the drainage pattern in this sector will create new conditions with an increased flow of natural and artificial tributaries from the headwaters of the basin that will produce exponential perturbations, due to the continuous remobilization of saline groundwater.

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