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Geochemical Mechanism Controlling Pampasic Ponds Hydrochemistry: Salado River Drainage Basin, Argentina

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ABSTRACT

Chemical analyses of major ions performed in some of the Pampasic ponds located in the lower reach the Salado River showed a similar composition to that of shallow groundwater, i.e., the total dissolved solids ranged between 1 g/l and 2 g/l, sodium was the most abundant among the cations and accounted (meq/l) for 80.6%. Calcium amounts were 6.5% while magnesium was 9.9%. Potassium was less abundant with a mean value of 3.0%. Appreciable differences between summer and winter values were not observed.

Since groundwater was the main source of surface water, a possible geochemical mechanism was proposed in order to achieve better understanding of the Pampasic pond's water chemistry. The processes that seem to be responsible for groundwater hydrochemistry are: cation exchange, ancient marine sediments dissolution and aluminosilicate weathering.

The differences observed between surface water and shallow groundwater composition with respect to an additional enrichment in sodium may be attributed to the evaporation-crystallisation process promoting calcite precipitation.

Keywords: salinity; cation exchange; aluminosilicate weathering; dissolution; pampasic ponds.

INTRODUCTION

From the geological point of view, the Salado basin contains Cretaceous, Tertiary (Lower and Upper), Plio-Pleistocene and Pleistocene (Medium and Upper) sediments superimposed over the Precambrian crystalline basement. The Plio-Pleistocene sediments of the Pampean Formation are a succession of silt-stones and fine sandstones with a relatively homogeneous mineralogical composition, consisting primarily of plagioclase, quartz and volcanic glass. Amphiboles and pyroxenes dominate the heavy mineral fractions, with montmorillonite and illite comprising the main clay minerals. The pampean loess composition also reveals an 8% of calcium carbonate as calcite (Teruggi, 1957). Such sediments have generally been regarded as eolian in origin, being derived from volcaniclastic deposits outcropping in the Andes over 1000 km to the west, although localized fluvial and mass movement processes probably redistributed the material to a large extent once accumulated in the Pampas (Kemp and Zárate, 2000). The sedimentary sequence continues with Post Pampean deposits of the recent Holocene age, mainly of marine and eolic origin in the depressed areas (Fidalgo, 1973).

Pampa Deprimida has wet climate and mean temperature between 13 - 16ºC. Mean annual precipitation is between 850 and 950 mm. Although precipitation is higher in summer, the precipitation-evaporation balance is negative in this season. The region is characterized by a very mild slope (0.3%) and extremely low morphogenetic potential that makes the runoff difficult during flooding periods. Infiltration and evapotranspiration are the principal components of the hydrological cycle (Sala, 1975).

The Pampasic ponds under study are located between 35º30′ - 35º56′ S and 57º45′ - 58º15′ W in the lower stream bed of the Salado River drainage basin, in the geomorphologic unit called Pampa Deprimida (Figure 1). The main characteristics are those of the low topographic slope great plain areas: surface geologic monotony; little tectonic deformation; predominance of thin sediments (clays and silts) over coarse ones (sand sediments) and continuity and areal extension of the geological units (Auge et al., 1983).

The ponds under consideration are Vitel, Chascomús, del Burro, Adela, Chis-Chis, Las Enca-

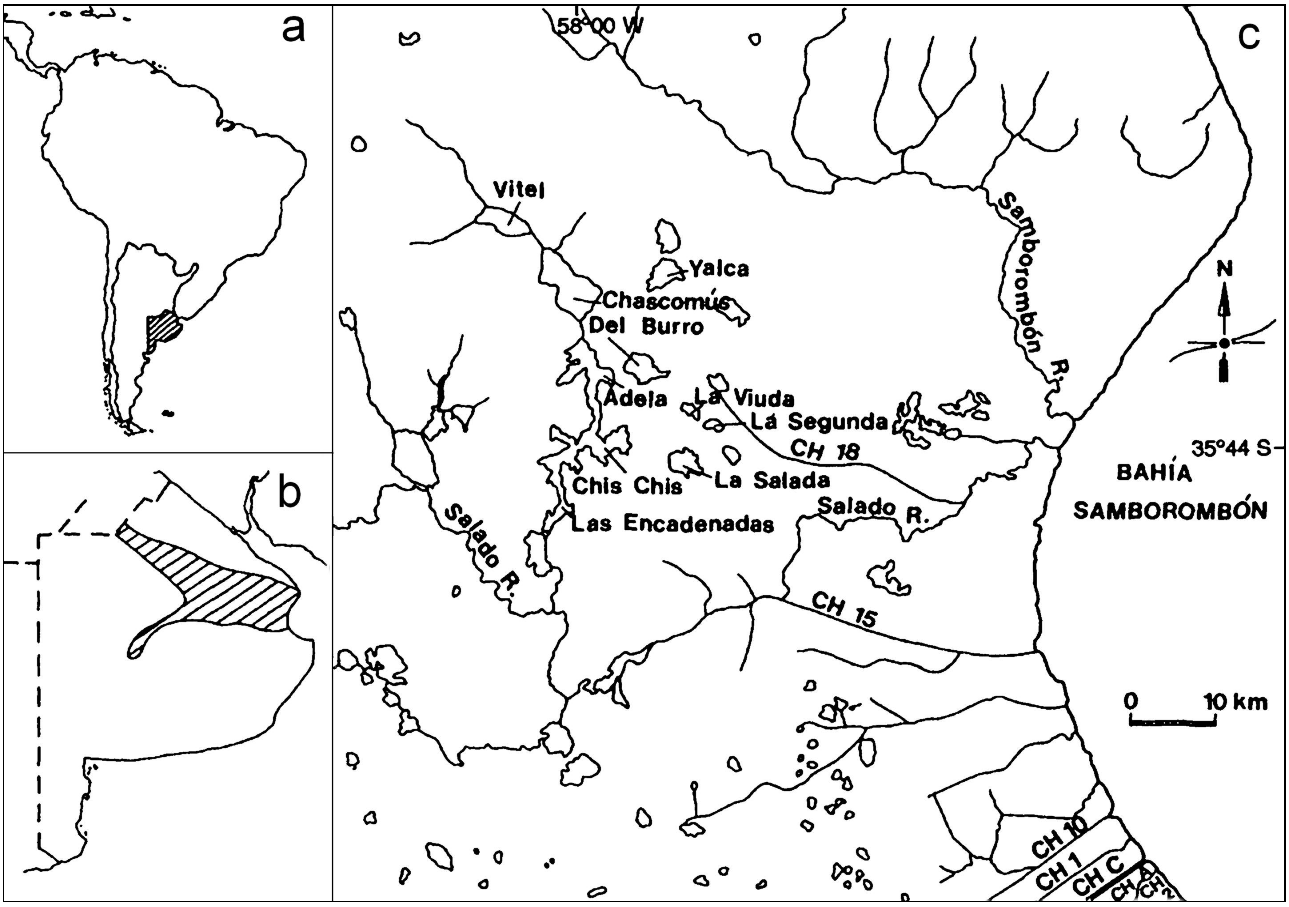

Figure 1. a. South America, Argentina, Buenos Aires Province; b. Buenos Aires Province and Salado River drainage basin; c. Pampasic ponds under study in the lower Salado River drainage basin (CH: channel).

denadas, which belong to the interconnected system called "Sistema de Las Encadenadas de Chascomús", La Segunda, La Salada and La Viuda. Pampasic ponds are permanent, lentic and shallow water bodies of different origin (combined fluvial and eolic processes), but without lakes as predecessors. They present a maximum depth of 4 m and a typical profile of pfanne or wanne. They are alkaline, and show a high trophic degree. Upper sediments are sandy silt, silt and clayey silt, with a calcium carbonate content between 1 and 20% and organic matter lower than 15% (Dangavs, 1998). Continuous vertical mixing, without thermal and chemical stratification, promotes high suspended particulate matter to prevent light penetration and an oxygenated environment even near the bottom, evidenced by high dissolved oxygen through all the water column (Ringuelet et al., 1968; Ringuelet, 1972).

The local groundwater drainage supplies the base discharge of pampasic pond's waters and holds the perennial discharge of stream beds (Sala et al., 1983). Therefore, it is necessary to study the geochemical processes that affect the groundwater chemistry in order to a better understanding of surface water chemistry. Chemical reactions in the edafic zone involve the dissolution and redistribution of CO_2 (g). Acidic rainwater with pCO_2 of about $10^{-3.5}$ atm. moves downward, and rapidly dissolves CO_2 due to root and microbial respiration and to a lesser extent to oxidation of organic matter, which occurs in soils at partial pressures larger than the atmospheric value ($10^{-1.5}$ - 10^{-2} atm). One direct result of dissolving CO_2 in water is a rapid increase in the carbonic acid content and a decrease in the pH. Another important soil zone atmospheric process is the dissolution of O_2 (g), resulting in levels of dissolved oxygen enough to control the redox chemistry in shallow groundwater (Drever, 1997).

Groundwater is able to dissolve halite sediments originated in Holocene marine intrusions (Querandino) that contribute to high salinity values and to sodium and chloride equivalent

Table 1. Physical and chemical parameters of aquatic systems under study.

ponds	pH	TEMP °C	TDS ppm	Na meq/l	K meq/l	Ca meq/l	Mg meq/l	Cl meq/l	CO3 meq/l	HCO3 meq/l	SO4 meq/l
Chascomús (W)	8.30	12.9	1626.4	20.05	0.49	1.43	2.22	11.75	<0.05	7.90	4.40
Chascomús (S)	9.47	21.7	1572.4	19.91	0.39	0.99	2.02	10.23	1.77	5.72	5.82
El Burro (W)	8.40	12.4	1612.3	19.59	0.47	1.43	2.96	12.81	<0.05	7.25	3.80
El Burro (S)	9.49	24.5	1342.1	17.17	0.42	1.00	2.14	9.92	3.97	4.84	2.15
Chis - Chis (W)	8.39	13.2	1292.7	14.64	0.43	1.92	2.37	9.54	<0.05	6.54	2.80
Chis - Chis (S)	8.83	27.5	1042.2	10.56	0.46	1.75	1.56	6.80	0.302	6.16	1.60
Las Encadenadas (W)	6.85	13.2	1200.2	12.93	0.51	1.64	2.32	7.78	<0.05	6.12	3.60
Las Encadenadas (S)	8.24	29.1	2388.4	28.37	0.82	2.70	4.77	20.5	0.87	7.48	7.80
La Salada (W)	8.17	14.6	1017.6	11.61	0.68	0.57	1.19	6.23	<0.05	7.67	0.20
La Salada (S)	10.33	26.2	999.8	14.13	0.64	0.35	0.99	7.33	4.84	3.52	0.40
La Segunda (W)	8.81	13.6	1012.4	11.50	0.81	1.07	1.38	7.89	0.91	5.93	0.20
La Segunda (S)	8.88	25.0	1104.7	13.00	0.87	0.90	1.32	8.14	0.44	6.93	0.20
Chascomús (W)	8.30	14.5	1536.6	18.53	0.51	1.39	2.07	10.98	<0.05	7.47	4.00
Chascomús (S)	9.22	23.0	1568.6	20.26	0.59	0.85	1.89	12.05	1.36	5.89	4.40
Vitel (W)	8.10	13.6	1007.0	10.67	0.32	1.35	1.14	5.03	<0.05	6.80	2.40
La Viuda (W)	9.50	15.5	1228.0	15.23	0.72	0.71	1.78	8.70	3.62	6.34	0.20
Adela (W)	8.12	12.6	1679.5	19.82	0.51	1.92	2.96	13.20	<0.05	8.01	3.60

S: summer; W: winter

amounts. Also promotes dissolution of carbonates, hydrolysis of aluminosilicates and volcanic glasses and formation of clays (montmorillonite and montmorillonite-illite interlayer). As a consequence, both the alkalinity and the cation concentration increase, mainly reflected in an increase of TDS of calcium bicarbonate type. Once in the saturated zone, if the groundwater is not yet in equilibrium with carbonate, silicate and aluminosilicate mineral, they will continue to dissolve. A cation exchange process taking place in the pampean loess sediments present in the Salado River has been proposed (Miretzky et al., 2000).

The aim of the present paper is to verify the occurrence of this process not previously mentioned as influencing pampasic pond's hydrochemistry. The global knowledge of the geochemical processes that control water chemistry composition will help to predict the ecosystem's response to increasing anthropic activities and contribute to the sustainability of this catchment area of high economic relevance in our country.

MATERIALS AND METHODS

The ponds water samples were collected from the surface of a pelagic zone during February (summer) and August (winter) 1998, as previously described (Miretzky et al., 2000). Groundwater samples were collected in the same periods and localized by GPS (Geographic satellital position). Local rain water samples were only available in the neighbourhood of Chascomús pond in june, july and august 1998. Temperature and pH were determined in the field by means of a portable pH meter Hanna HI 9025. Once in the laboratory, the samples were filtered using 0.45 microns acetate cellulose membrane Micro Separations Inc. (MSI), and were stored in polyethylene bottles. All samples were taken in duplicate.

Major ions in surficial, groundwater and local rainwater were determined by conventional methods: carbonates and bicarbonates by acid titration, chloride by $AgNO_3$ titration, sulphate by precipitation titration with $BaCl_2$ and sodium rodizonate as an indicator in water-acetone medium; Na and K were determined by atomic spectrophotometric emission and Ca and Mg by atomic spectrophotometric absorption (Varian Techtron Model AA275). Silica was determined spectrophotometrically at 815 nm (1 cm path length Jasco 7850 spectrophotometer) after reduction of silicomolybdate in acidic solution to "heteropoly blue" by ascorbic acid (APHA, 1993). Determinations were performed in duplicate being the relative error < 1.0% and the electroneutrality condition (Appelo y Postma, 1993) E.N.% was < 2% for all of them.

Table 2. Chemical composition of 3 rainwater samples from Chascomús region.

	Na ppm	K ppm	Ca ppm	Mg ppm	Cl ppm	HCO_3 ppm	SO_4 ppm	TDS ppm
June-98	2.05	0.26	0.13	0.31	3.82	0.15	0.48	7.20
July-98	2.07	0.25	0.12	0.32	3.95	0.15	0.49	7.35
August-98	1.95	0.26	0.13	0.29	3.91	0.15	0.49	7.18
mean value	2.02	0.26	0.13	0.31	3.89	0.15	0.49	7.24
St. Dev.	0.06	0.01	0.01	0.02	0.07	0.00	0.01	0.09

Total dissolved solids (TDS) were calculated, as usual, as the sum of the above ion concentrations, since they account for most of the dissolved salts.

The balance precipitation-evaporation was calculated by the BALUBA 1.0 (1991).

RESULTS AND DISCUSSION

The average value of TDS for all the analysed ponds was 1366.5 ppm. Ionic composition (meq/l) (Table 1) showed that chloride and bicarbonate were the most abundant anions. The former presented a conservative character since it amounted to 47.8% in summer and 48.7% in winter. Bicarbonate showed a significant difference between summer and winter, with a mean value of 28.6% and 37.4%, respectively. Sulphate's behaviour was similar to chloride's with a summer value of 12.8% and a winter value of 12.3%. Sodium was the most abundant among the cations and accounted (meq/l) for 80.6%. Calcium amounts were 6,5% while magnesium were 9.9%. Potassium was less abundant with a mean value of 3.0%. Appreciable differences between summer and winter values were not observed (Table 1).

Precipitation-evaporation balance during the sampling period (summer 1998 - winter 1998) evaluated with the computer program BALUBA 1.0 (1991) (data not included) was about +200 mm, but this dilution effect was not appreciable on ion concentration, since all ions considered showed a conservative character with the exception of bicarbonate. HCO_3 concentration (% meq/l) increased 27% between summer and winter, but this fact may be explained by the displacement of carbon dioxide due to the temperature variation (25.2°C - 13.6°C) and by summer photosynthetic activity, important in these ponds because of their high trophic degree. As an example, according to Conzonno and Clav-

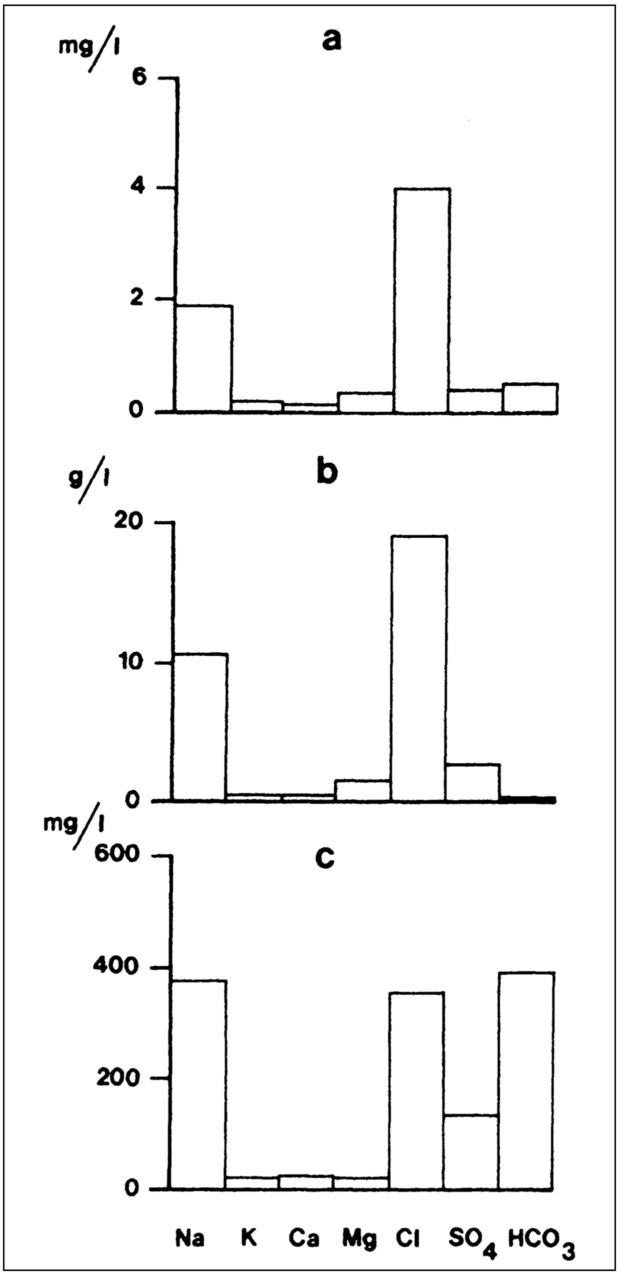

Figure 2. Mean ionic concentration: a. rain water, b. sea water; c. pampasic ponds.

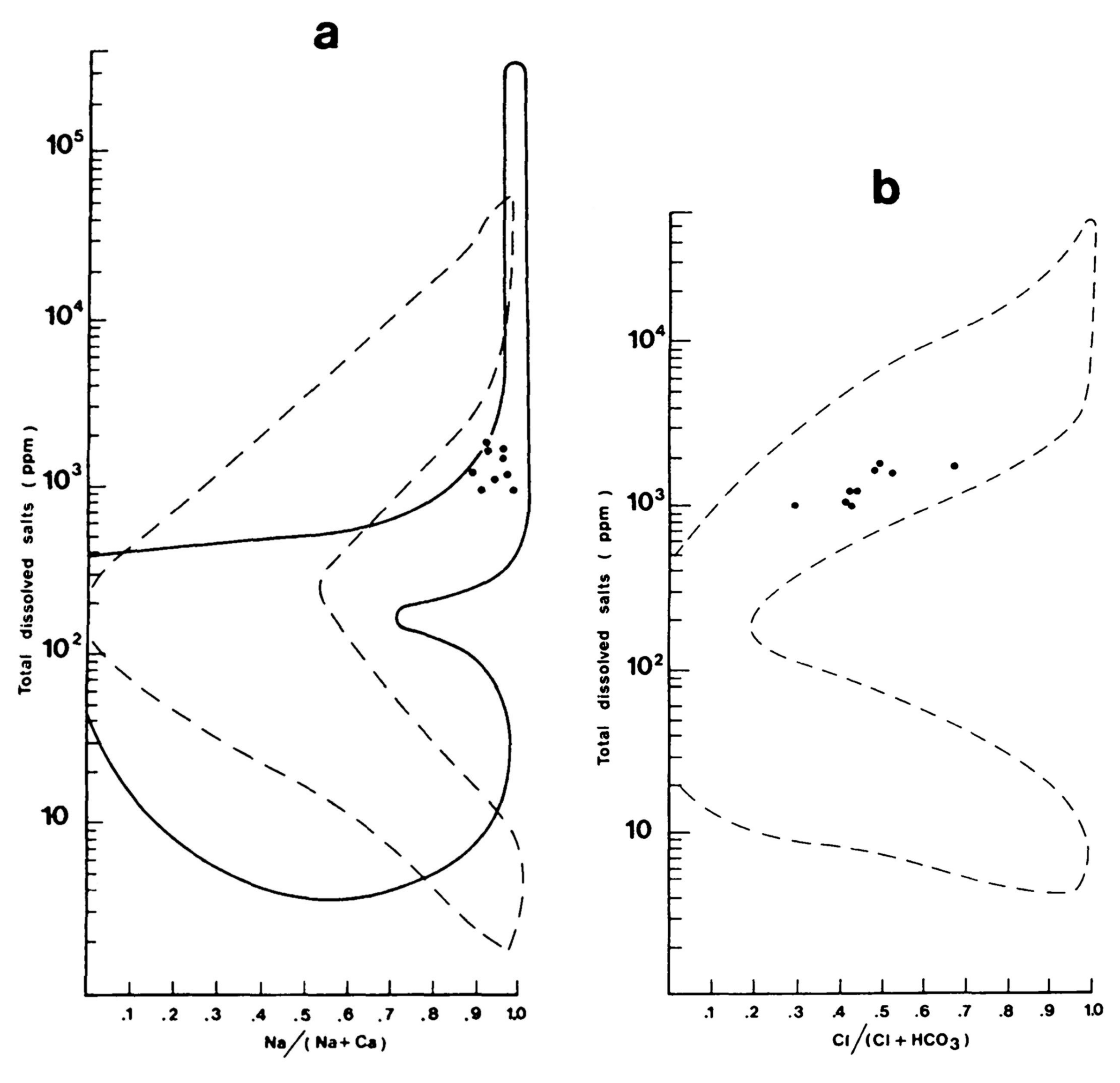

Figure 3. Pampasic ponds anual Gibb's diagram: a. cationic; b. anionic.

erie (1987/8), primary production in Chascomús pond was 24.3 and 164 mg C/m^{3}h in winter and summer respectively. Therefore, the increase of bicarbonate in winter is associated to the displacement of carbonate to bicarbonate. Moreover, HCO_3^- plus CO_3^{-2} showed a conservative character.

As it was expected, local rainwater composition (Table 2) is similar to seawater composition (Custodio and Llamas, 1976; Livingstone, 1963) in relation to sodium, chloride, magnesium and sulphate ratios, and this may be explained by the fact that the area under study is near the Atlantic Ocean coast (50 km). In the period sampled, local rainwater TDS value was 7.8 ppm while sea water average TDS value is 35 g/l (Figure 2a, b). It can be seen (Figure 2c) that considering mean anual concentration values from Table 1, Pampasic ponds also present similar ionic ratios. Nevertheless, taking into account that pampasic ponds' TDS values lie between 1 g/l and 2 g/l, it seems that atmospheric precipitation is relatively unimportant in determining the content of dissolved salts.

Table 3. Shallow groundwater chemical composition. Summer, 1998.

M	Lat S	Long W	T °C	pH	SIO2 ppm	Na meq/l	K meq/l	Ca meq/l	Mg meq/l	Cl meq/l	SO4 meq/l	CO3 meq/l	HCO3 meq/l	STD ppm
P2	35°52′	57°55′	17.7	7.85	70.5	10.83	0.77	4.19	3.95	5.50	1.21	-	12.31	1553.5
P3	35°52′	57°55′	18.8	8.10	54.9	24.96	0.64	1.16	2.23	10.97	4.18	0.43	12.05	2155.0
P4	35°54′	57°59′	17.9	7.56	60.7	19.09	1.62	4.45	5.74	11.26	4.75	-	13.95	2270.1
P5	35°55′	57°57′	21.0	8.04	60.3	18.43	0.68	3.69	5.46	12.83	2.39	0.43	10.56	1945.4
P7	35°40′	57°57′	19.2	6.95	63.1	27.17	0.77	5.89	5.60	18.43	7.20	-	13.20	2768.0
P8	35°40′	57°57′	21.6	7.34	19.6	11.30	0.64	2.89	2.14	3.64	1.19	-	12.26	1353.6
P9	35°34′	58°01′	19.3	6.85	65.4	21.20	0.49	1.20	2.80	9.17	4.39	-	11.00	1918.6
P10	35°34′	58°01′	22.7	7.23	72.9	17.35	0.46	0.45	2.80	6.04	0.79	-	11.51	1651.9
P11	35°32′	58°01′	20.2	7.15	63.1	4.59	0.51	2.90	2.55	1.58	0.40	-	8.07	885.1
P12	35°34′	57°58′	22.3	7.99	68.6	14.91	0.31	0.35	0.49	2.88	0.79	-	11.70	1325.7
P13	35°32′	58°11′	21.4	7.85	63.1	11.87	0.31	0.30	0.58	1.58	1.39	-	10.12	1127.6
P14	35°32′	58°11′	19.5	7.26	68.2	10.20	0.64	0.90	3.13	1.60	0.79	-	10.50	1237.4
P15	35°32′	58°11′	22.0	7.85	61.1	9.40	0.33	0.75	0.82	1.05	1.21	-	8.80	981.9
P16	35°28′	58°08′	24.2	7.64	67.0	9.57	0.43	0.70	1.15	1.30	0.40	-	9.67	1012.0
P17	35°46′	57°56′	18.8	6.63	63.5	12.22	1.10	6.84	6.01	17.29	1.21	-	7.04	1722.8
P18	35°42′	57°57′	19.0	9.10	63.5	15.52	0.69	1.10	2.63	5.75	1.60	3.53	9.24	1461.9
P19	35°37′	58°10′	20.4	8.18	53.7	9.74	0.41	0.89	1.15	1.57	1.20	0.44	8.91	1020.6
P20	35°40′	58°08′	17.7	7.56	63.1	22.26	0.41	0.70	1.23	3.12	3.59	-	17.64	2050.1
P21	35°43′	58°07′	17.5	7.15	63.1	17.04	0.54	2.45	2.80	3.12	2.39	-	16.43	1905.0
P22	35°45′	58°06′	18.1	8.13	63.1	16.79	0.26	0.55	0.82	2.62	1.60	0.18	13.90	1507.9
P23	35°48′	58°04′	18.0	7.89	63.1	6.87	0.72	2.70	2.96	1.83	1.00	-	10.12	1093.2
P24	35°48′	58°05′	21.5	8.07	68.2	4.17	1.28	4.95	4.77	2.62	1.20	-	11.00	1209.5
P25	35°53′	58°05′	21.6	8.89	64.9	9.30	0.59	1.60	1.48	1.05	1.20	1.32	9.24	1054.6
P26	35°50′	58°08′	22.8	8.40	61.1	11.48	0.64	2.00	2.39	2.62	1.60	0.18	11.70	1336.8
P28	35°44′	57°52′	18.4	7.02	63.3	15.22	0.84	5.04	3.95	15.19	0.80	-	8.80	1714.8
P29	35°43′	57°52′	21.9	8.20	49.1	9.91	0.56	2.45	1.81	2.62	0.80	0.18	10.82	1171.7
P30	35°48′	57°47′	18.2	7.88	63.3	17.78	0.62	0.49	0.93	3.99	1.00	-	15.40	1646.4
P31	35°50′	57°45′	17.7	6.98	67.8	17.78	0.61	1.59	2.34	7.09	2.00	-	12.30	1737.7
P32	35°45′	57°48′	15.8	7.43	72.2	18.09	0.31	0.66	0.97	4.16	1.98	-	13.94	1637.3
P33	35°55′	57°51′	18.4	7.89	58.5	12.30	0.69	1.55	1.56	3.93	1.00	-	10.95	1283.7

Table 4. Shallow groundwater chemical composition. Winter, 1998.

M	Lat S	Long W	pH	T °C	SIO2 ppm	Na meq/l	K meq/l	Ca meq/l	Mg meq/l	Cl meq/l	SO4 meq/l	HCO3 meq/l	STD ppm
P104	35°54′	57°59′	7.55	13.8	66.2	21.11	1.51	2.71	3.74	11.21	4.00	13.60	2174.8
P108	35°40′	57°57′	7.05	16.0	68.5	13.19	0.47	3.21	3.75	5.26	3.20	11.78	1593.7
P116	35°27′	58°08′	6.60	11.8	70.9	6.79	0.43	1.64	1.53	1.60	0.40	8.79	917.7
P119	35°37′	58°10′	6.39	12.7	68.8	8.41	0.43	1.00	1.14	1.26	0.20	9.06	924.6
P120	35°40′	58°08′	6.75	15.6	60.8	18.57	0.45	0.68	1.14	2.97	2.00	16.07	1724.5
P128	35°44′	57°52′	7.25	17.3	68.8	17.37	1.02	5.20	4.35	18.65	1.20	7.70	1863.8
P131	35°50′	57°45′	7.85	16.8	66.4	17.67	0.77	2.28	2.86	8.01	2.40	13.43	1906.4
P133	35°55′	57°51′	7.41	17.0	63.4	10.34	0.51	1.92	1.48	2.86	1.20	10.00	1152.0
P134	35°33′	58°10′	6.61	12.2	72.2	2.27	0.49	2.14	2.77	0.57	0.20	7.27	698.4
P135	35°32′	58°06′	6.75	13.9	73.6	18.95	0.74	4.56	5.28	12.70	6.80	10.19	2097.6
P136	35°35′	58°02′	6.75	13.5	61.1	17.67	0.38	1.50	1.58	6.18	3.60	11.24	1614.0
P137	35°46′	58°06′	6.15	13.3	63.9	12.71	0.57	1.50	1.43	2.29	0.60	13.61	1376.1
P138	35°49′	58°05′	6.30	13.8	70.5	5.60	0.77	3.61	3.46	3.43	0.80	9.20	1266.8
P139	35°52′	58°04′	6.76	14.3	63.9	17.89	0.51	1.60	2.37	9.61	2.00	10.65	1647.3
P140	35°39′	58°09′	6.67	14.7	58.6	14.23	0.43	0.68	0.79	1.60	1.60	13.14	1365.7
P141	35°38′	57°57′	8.49	13.4	63.6	12.93	0.81	2.64	2.37	4.58	2.40	11.30	1466.2
P142	35°39′	57°55′	8.46	13.5	71.7	10.03	0.85	3.85	5.14	7.99	1.60	9.65	1670.2
P143	35°40′	57°54′	7.88	16.1	62.1	10.80	0.51	1.00	0.89	1.83	0.60	11.33	1155.8
P144	35°48′	57°47′	7.11	16.3	64.8	5.25	1.28	6.00	6.78	5.83	2.00	11.86	1708.7
P145	35°50′	57°46′	7.50	14.0	67.5	6.53	0.64	2.00	2.57	1.72	1.00	9.25	1011.8
P146	35°52′	57°45′	7.85	15.6	62.1	6.53	0.72	1.92	2.57	2.29	0.80	8.61	999.9
P147	35°50′	57°47′	7.25	16.5	67.5	15.44	0.68	1.71	2.47	6.75	2.40	11.55	1577.7
P148	35°51′	57°48′	7.31	15.6	61.3	3.07	0.64	2.21	2.47	0.80	0.20	7.70	763.8
P149	35°51′	57°49′	7.68	15.2	58.2	19.40	0.55	0.57	0.99	3.10	0.40	18.29	1799.4
P150	35°50′	57°51′	7.91	15.3	61.5	26.73	0.85	1.28	2.86	15.33	4.00	12.23	2261.8
P151	35°49′	57°49′	7.46	16.5	62.1	8.53	0.81	2.92	3.75	4.28	1.60	9.78	1259.0
P152	35°40′	57°57′	7.37	14.7	63.6	34.46	1.15	5.56	8.59	34.56	5.20	9.83	3196.2
P153	35°46′	57°57′	8.18	16.7	69.3	15.51	1.06	6.70	7.70	15.26	2.00	13.05	2274.0
P154	35°49′	57°59′	8.10	19.3	65.3	28.63	0.60	1.00	2.77	15.10	4.80	13.14	2373.0
P155	35°50′	57°59′	7.57	19.4	66.4	30.59	0.47	0.71	1.98	11.04	4.40	18.61	2604.4
P156	35°53′	57°58′	7.60	16.6	58.8	26.31	0.77	2.50	3.33	8.82	2.80	21.09	2554.0
P157	35°54′	57°58′	7.86	15.6	64.9	9.70	0.47	2.00	1.98	2.75	1.00	10.42	1176.2
P158	35°55′	58°01′	7.56	17.2	64.9	9.80	0.44	2.25	1.81	2.91	0.95	10.61	1175.6
P159	35°54′	57°54′	7.69	16.6	64.9	14.00	0.77	0.86	1.78	6.11	1.60	9.72	1376.6
P160	35°57′	57°54′	7.52	16.9	59.5	17.70	0.98	2.14	2.67	8.23	3.80	11.36	1779.9
P162	35°35′	57°57′	7.85	18.4	64.9	9.03	0.21	1.07	1.78	1.83	0.80	9.51	1012.7
P163	35°33′	57°59′	7.87	18.0	66.7	13.04	0.21	0.14	0.20	1.37	1.00	11.33	1212.9

Gibbs (1970) concluded that three natural mechanisms control the chemistry of surface waters: atmospheric precipitation, rock dominance or rock weathering, and evaporation-crystallisation process. Gibbs' diagram, a boomerang shape 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, the chemical composition of surface waters depends on the climate, the geomorphology and the chemical composition of the parental rocks in the basin. In a general way, waters dominated by this process present calcium and bicarbonate as predominant ions, TDS values are medium, 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. Rainwater can be considered 1000 times diluted seawater, with sodium the dominant cation, the weight relation Na^+ / (Na^+ + Ca^{2+}) near 1.0 and low TDS value. Surface waters with chemical composition responding to this process will be in the right bottom side of the boomerang. It is probable that these waters will correspond to high rainfall areas, with no significant relief and where the amount of dissolved salts derived from rock weathering process is not significant.

These 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-crystallisation 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 in the right upper side of Gibbs boomerang in a continuous series between those whose chemical composition is derived from rock weathering and sea water composition. Changes in composition as a consequence of changes in biota and relief are minor in comparison with those due to the three processes mentioned before.

When the weight relation Na^+/(Na^+ + Ca^{2+}) is plotted against TDS values for the pampasic ponds waters under study (mean anual concentrations were considered), it can be observed that data lie outside the boomerang (Figure 3a). Na^+ / (Na^+ + Ca^{2+}) values lie between 0.9 and 1.0 and TDS values between 1.0 y 2.0 g/l. This means that rock weathering and evaporation-crystallization processes alone, are unable to explain the chemical characteristics of surface waters. Also, we can observe that no data plot in the bottom right side of the boomerang, meaning that atmospheric precipitation is not an important process in determining the chemical composition of these waters, although the hydrological balance is positive in this region.

Wetzel (1983) modified Gibbs' diagram, but he only changed the boundaries delineating the dominant processes and not the assumptions on which the model is based. Wetzel's diagram consists in an envelope shaped like an alchemist's retort rather than a boomerang.

Kilham (1990), studied the mechanisms controlling African surface water chemistry, determining that chemical composition is largely controlled by rock weathering, evaporative concentration and calcite precipitation. Concentrated waters (TDS values > 1.0 g/l) plot outside the boomerang envelope. He concluded that deviations from the basic pattern are caused by the contamination with salts from ancient lacustrine deposits of marine origin which are transported by ocean derived atmospheric precipitation (cyclic salts), leached from rocks or dissolved from evaporite deposits. African waters fit better Wetzel alchemist's retort. We can observe that pampasic ponds waters also fit better in Wetzel retort (Figure 3a).

Drago and Quiros (1996) reported the hydrochemistry of inlands waters in Argentina finding deviations from the Gibbs basic pattern. They concluded that chemical composition is largely controlled by rock weathering and evaporative concentration and deviations are due to dissolution of ancient marine salts.

Since the amount of Na^+ (meq/l) is larger than that of Cl^-(meq/l), the dissolution of ancient salts of marine origin cannot be the only explanation of the deviations from Gibbs diagram, since halite dissolution would provide equal amounts of both ions. Therefore, we proposed a cation exchange process taking place in the pampean loess sediments, not previously described in this region (Miretzky et al., 2000). To confirm our proposal, local shallow groundwater was analysed in order to determine the outstanding geochemical processes determining its chemical characteristics.

Shallow groundwater chemical composition in the two periods sampled can be observed in Table 3 and Table 4. In summer, sodium among the cations (in meq/l) accounted for 71.9%, calcium for 11.5% and magnesium for 13.4% and among the anions, bicarbonate for 59.4%, chloride for 27.51% and sulphate for 8.6%. In winter, sodium accounted for 69.0%, calcium for 12.5% and magnesium for 14.9%, bicarbonate for 61.8%, chloride for 29. 2% and sulphate for 9.0%. No significant differences between summer and winter values are observed.

SiO_2 amounts in groundwater are nearly 65 ppm, evidencing an aluminosilicate weathering process taking place in the Salado River drainage basin. This significant value has not been previously reported in this area, but similar contents on the same aquifer but in the southeast of the Buenos Aires Province have been reported (Martinez and Osterrieth, 1999). There are no unequivocal weathering reactions for the silicate minerals. Depending on the nature of parent rocks and hydraulic regimes, different secondary minerals are formed as reaction products (kaolinite, smectite, illite, gibbsite). In all cases, water and carbonic acid (biogenic origin) are the main reactants, being the net result of the reaction the release of alkaline cations, the increase of alkalinity as HCO_3^- is formed, and production of H_4SiO_4.

The clay minerals present in pampean loessic sediments are mainly illitic and montmorillonitic with kaolinite as a subordinate constituent (Teruggi, 1957). When a sodium clay (montmorillonite cation exchange capacity = 80 meq/100 g) interacts with a solution in which calcium is the predominant ion, each couple of absorbed sodium ions is replaced by a solubilized calcium, turning groundwater enriched in sodium, changing from a calcium bicarbonated type into a sodium bicarbonated type. Therefore, when groundwater reaches the ponds, and being its main source, pond's waters become enriched in sodium. This process increases the weight relation Na^+ / (Na^+ + Ca^{2+}) values and data plot outside Gibbs boomerang.

To corroborate this cation exchange process, winter and summer groundwater chemical data were analysed by means of the Chebotarev diagram presented in Figure 4a, b. This figure represents the percentages of bicarbonate ions in the bottom side of the figure against the sum of chloride and sulphate percentages in the upper side, and the percentages of sodium and potassium on the left side against calcium and magnesium percentages on the right side. There is an hypothetical line of mixing between fresh water and seawater (or marine sediments). The alterations with respect to the line of mixing should be interpreted as being due to another processes primarily affecting the cation composition. A vertical displacement with respect to the mixing line can be attributed to both direct and inverse cationic exchange. As it can be seen in Figure 4, groundwater samples plots are displaced towards positions that represent an increase in Na^++ K^+ percentages and a decrease in Ca^{2+}+ Mg^{2+} percentages, with respect to the hypothetical line, supporting the hypothesis that the groundwater is involved in a direct process of cationic exchange confirming our previous proposal.A comparison between surface water and shallow groundwater composition (Table 5) shows an additional enrichment in sodium, chloride and sulphate that may be attributable to the evaporation-crystallisation process promoting calcite precipitation. This fact accounts for the diminution in calcium concentation. The difference observed in silica values may be explained by the Si uptake by diatoms, being this biogeochemichal process important in pampasic ponds because of their high eutrophic degree (Izaguirre and Vinocur, 1994).

Table 5. Comparisson between surface water and groundwater composition.

	Surface water mean value (meq/l %)	Shallow groundwater mean value (meq/l %)
Chloride	48.2	28.4
Sulphate	12.7	8.8
Sodium	80.6	70.5
Potassium	3.3	3.2
Calcium	6.5	12.0
	ppm	ppm
Silica	2.5	63.50

On the other hand, the weight relation $Cl^-/(Cl^- + HCO_3^-)$ (x-axis) was plotted against TDS values (y-axis) for pampasic pond waters (Figure 3b). Gibbs diagram shows that data plot inside the boomerang shape envelope in the upper side, being rock weathering and evaporation-crystallisation processes the ones controlling hydrochemistry. No data plot in the bottom 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 determinining the deviation from the Gibbs basic pattern, this deviation should also be observed in the anionic diagram.

These results confirm 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.

CONCLUSIONS

The principal processes taking place in the Salado River drainage basin responsible for the Pampasic ponds hydrochemistry are: dissolution of halite sediments originated in Holocene marine intrusions that results in high equivalent amounts of sodium and chloride; aluminosilicate weathering that results in a release of mainly, sodium, calcium, magnesium, potassium, bicarbonate and silica and the cation exchange process in the loessic sediments, that promotes an extra enrichment in sodium. These processes ocurr in the evolution path from rainwater to groundwater being this, one of the sources of surface water, whereas in the latter the evaporation-crystallization process promoting calcite precipitation and an additional enrichment in sodium is the principal one. Also, the difference observed in dissolved silica values between groundwaters and surface waters, is linked to Si uptake by diatoms.

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O Mecanismo Geoquímico Controlador da Hidroquímica das Lagoas do Pampa, Bacia de Drenagem do Rio Salado, Argentina

RESUMO

Análises químicas dos íons importantes, realizadas em algumas das lagoas do pampa que ficam no curso inferior do rio Salado, apresentaram uma composição semelhante àquela da água subterrânea rasa, isto é, sólidos dissolvidos totais que variavam de 1g/l a 2g/l. O sódio foi o cátion mais abundante e era responsável (mEq/l) por 80,6%. As quantidades de cálcio eram de 6,5%, enquanto que o magnésio era 9,9%. O potássio era menos abundante, com um valor médio de 3,0%. Não foram encontradas diferenças significativas entre os valores de verão e de inverno.

Como a água subterrânea era a principal fonte superficial, foi proposto um possível mecanismo geoquímico a fim de entender melhor a química hídrica da lagoa. Os processos aparentemente responsáveis pela hidroquímica são a troca de cátions, a dissolução de antigos sedimentos marinhos e o intemperismo de silicato de alumínio.

As diferenças observadas entre a composição de água de superfície e da água subterrânea rasa, quanto ao enriquecimento adicional de sódio pode ser atribuída ao processo de evaporação-cristalização que promove a precipitação de calcita.

Palavras-chave: salinidade; troca de cátions; intemperismo de silicato de alumínio; lagoas do pampa.