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Hydrochemical variability associated with rainfall regime: a case study in the coastal wetland of the outer Río de la Plata Estuary, Argentina

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Abstract In coastal wetlands, the interaction between groundwater, surface water and marine or estuarine water determines the water chemistry; variations in the water balance may be of influence as well. The objective of this work was to assess how the rainfall regime affects the hydrological and geochemical processes that regulate the quality of surface and groundwater in the Samborombón Bay coastal wetland. We analyzed the water balances and chemical data of surface and groundwater during a dry and a wet period. Results show that the rainfall regime regulates water quality in the three hydrological units defined for the region (i.e., groundwater in the coastal plain, groundwater in the shell ridges and surface water in the coastal plain). In the water balance corresponding to a dry period, real evapotranspiration is similar to precipitation. In such conditions, in the coastal plain, the halite and gypsum salts precipitate. Subsequently, the rain or the tidal flow dissolves them, and they enter the water table by infiltration. The lowering of the water table favors the oxidation of sedimentary pyrite and the contribution of sulfates. The oversaturation of calcium carbonates in groundwater causes their precipitation, both in the coastal plain and in the shell ridges. The chemistry of surface water depends on the influence generated by the tidal inflow and groundwater discharge. During the wet periods, precipitation is higher than real evapotranspiration, leading to the infiltration of water excess toward the water table and the increase in surface runoff; this causes a decrease in the concentration of ions dissolved by dilution. This rainfall regime hinders the formation of evaporite salts (gypsum and halite) and leads to the undersaturation of groundwater with respect to calcite, allowing the dissolution of carbonates. As regards the chemical composition of the surface water in the coastal plain, the surface runoff in the drainage basin is more significant than the groundwater discharge and the tidal inflow. It can be concluded that the alternation of dry and wet periods in the Samborombón Bay wetland causes the rainfall regime to be a determining factor in the different hydrological and geochemical processes affecting the quality of surface and groundwater.

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Introduction

What characterizes the complex hydrological dynamics of coastal wetlands is a significant interaction among groundwater, surface water and estuarine water (Cahoon et al. 2006; Manda et al. 2014). In regions such as bays and estuaries, it is possible for significant changes in sediment composition, water chemistry and biological characteristics to take place on a limited spatial and temporal scale (Bianchi 2006). The analysis of ion ratios by means of hydrogeochemical tests is a valuable tool in defining the

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geochemical processes that regulate water composition in coastal environments, e.g., the reactions deriving from water–sediment interaction (i.e., dissolution–precipitation, ion exchange and oxidation–reduction) (Marimuthu et al. 2005; Sola et al. 2012; Nasir and Harikumar 2012). It is also useful in determining the possibility of water contamination or mixtures (e.g., seawater intrusion and contribution from several aquifers) and in defining the sources of hydrological processes (Terzic et al. 2010; Patra et al. 2012).

The estuary of the Río de la Plata is a hydrological system of importance for the social, economic and ecological development of the coast of the Buenos Aires province in Argentina and of Uruguay. The Samborombón Bay wetland is located on the Argentine bank of the outer estuary and designated as a Ramsar site in 1997. This wetland is a feeding, resting and breeding area for migratory birds, and a reserve for endangered species (*Ozotoceros bezoarticus celer*). On the coast of the bay, the landscape of the intertidal plain has a particular appearance given by the fact that it is a densely populated crab habitat and is locally referred to as *cangrejal* (i.e., large muddy tidal flats covered by crab burrows). The most typical plant species in the wetland are Spartina, Salicornia and Zizaniopsis in the intertidal zone, while in the shell ridges and sandy layers—elevated areas with well-drained soils— there are tree specimens of *Celtis tala*. This vegetation has a significant role in the primary productivity of the region, as well as providing nesting places for several bird species, producing the detritus that provides the coastal substratum with organic matter and constituting the basis of the regional trophic webs (Canevari et al. 1998). The ecosystems of the wetland are strongly dependent on the hydrological conditions; the hydrochemical characteristics, in particular, are a factor determining species distribution.

The Samborombón Bay littoral has a humid temperate climate with an annual rainfall regime that shows alternating wet and dry periods (Carol et al. 2010). The hydrology of the area mainly depends on the rainfall regime and the tidal influence from the estuary (Carol et al. 2013). The objective of this work is to assess how the rainfall regime conditions the hydrological and geochemical processes that regulate the quality of surface and groundwater in the Samborombón Bay coastal wetland.
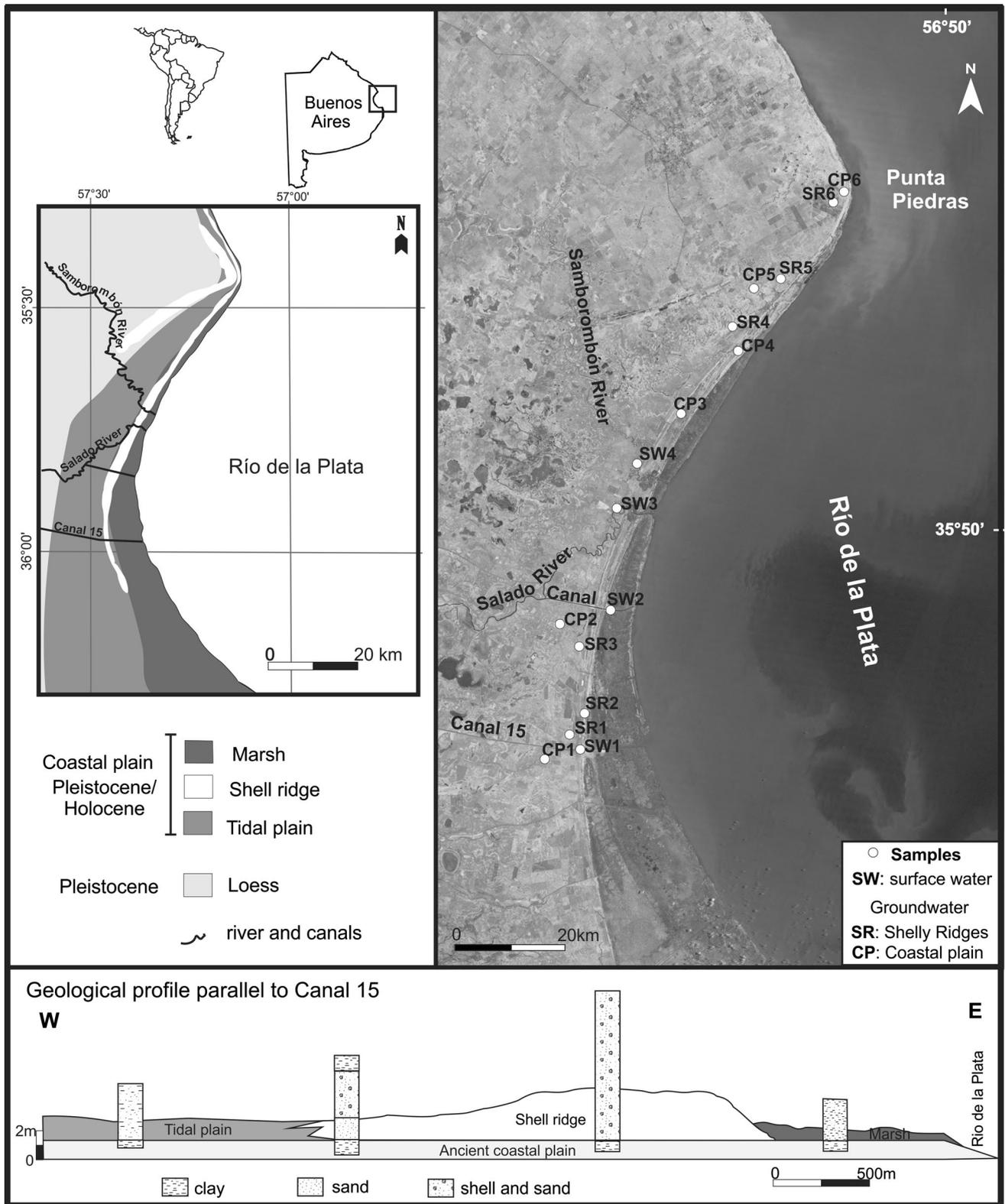
Study area

The Argentine margin of the outer Río de la Plata estuary comprises a coastline of approximately 180 km, which extends from Punta Piedras to Punta Rasa (Fig. 1). The dynamics of the Río de la Plata are the result of the

contribution of its main tributaries (i.e., the Paraná River and the Uruguay River) and of the oceanic tidal wave influence (Balay 1961). The predominance of either of the contributing sources in the different sectors of the estuary can be identified in the water salinity content. In the upper and middle sections of the Río de la Plata, salinity values are as expected for fluvial systems (0.2–2 g/L), while in the outer estuary, they suggest the presence of a mixing area with increasing salinity contents toward the ocean (Fig. 1). Salinities are about 3 g/L in the Punta Piedras area, whereas toward the south (Punta Rasa), the values are close to 20 g/L (Guerrero et al. 1997).

An extensive coastal plain in which shell ridges and sand sheets occur characterizes the study area (Fig. 1). Its geological and geomorphological configuration developed in the late Quaternary, as sea level oscillations caused a succession of shoreline displacements (Violante et al. 2001). Quaternary sediments can be observed in four different depositional environments in the coastal bay areas (Fidalgo et al. 1973; Fucks et al. 2008; Fig. 1). The oldest deposits occur in a low-energy coastal plain are characterized by an intertidal environment, composed of clayey to clayey–sandy sediments (i.e., "ancient coastal plain" in Fig. 1), whereas overlying sandy–silty sediments with clay intercalations of coastal plain environments are developed in the continental sectors (i.e., "tidal plain" in Fig. 1). There is an observable shift in the depositional conditions toward high-energy beach environments, which triggered the formation of shell ridges associated with storm conditions (i.e., "shell ridge" in Fig. 1). These elevated landforms consist of loose marine shell debris, and they alternate in patches with sand and clay layers. The composition of the sand is mainly quartzose, with a smaller quantity of basic plagioclase clasts. In the clay, the Na^+ is a dominant exchange ion originated by the seawater (Na–Cl) trapped in the sediment during the deposition of shell ridges (Carol and Kruse 2012). In the more littoral areas, the deposits of the present-day coastal plain gradually transform into a marsh environment, composed of silty clays with high organic matter content (i.e., "marsh" in Fig. 1). In the marsh, we detected the presence of pyrite in greenish clay levels associated with reducing conditions of the sediment (Carol et al. 2011).

The major watercourses flowing into the study area are the Samborombón River and the Salado River, which drain a large plain region of the Buenos Aires province (Fig. 1). Downstream, the low slope of the area (10^{-4}) complicates the natural drainage toward the Samborombón Bay, as the tidal inflow at high tide hinders it periodically. A considerable number of canals were built in the early twentieth century to enhance drainage, the most important ones being the Salado River relief canal and the Canal 15 (Fig. 1).

Fig. 1 Location of the study area and sampling points. Geological cross section (**a**, **b**) and hydrodynamic behavior of the hydrological units

Methodology

We carried out water balances for 2008 and 2009 (Thornthwaite and Mather 1957) on the basis of monthly temperature and rainfall data. Besides, in order to establish at a global level, the periods of water deficit and excess occurring in the region, the water balances considered the climate data of a more extended period (1909–2014).

We analyzed background data, field surveys, topographic maps and satellite images to study the geological and geomorphological features of the region. In order to collect samples of groundwater and surface water from the main canals and watercourses, we set up a monitoring network at a regional level (Fig. 1). The monitoring points include wind pumps and shallow exploration wells (between 5 and 10 m deep) distributed over the main hydrogeological units in the study area. We collected the samples during a dry and a wet period, and analyzed pH, electrical conductivity, calcium, magnesium, sodium, potassium, chloride, sulfate, carbonate and bicarbonate. The collection, preservation and chemical analyses of the water samples were carried out in accordance with the standard methods proposed by the American Public Health Association (APHA 1998): Na^+ and K^+ by flame photometry; hardness of $CaCO_3$, Ca^{2+}, CO_3^{2-}, HCO_3^- and

Cl^- by volumetric methods; Mg^{2+} on the basis of calcium and total hardness data; SO_4^{2-} by nephelometry; and the amount of total dissolved solids by gravimetry. We analyzed the samples at the chemical laboratory of the Universidad Nacional de La Plata (National University of La Plata). As regards electrical conductivity and pH, we measured them on-site immediately after sampling, using portable equipment.

Hydrochemical charts were used to analyze the results concerning major ion concentrations. In order to evaluate tidal influence, we used a mean chemical value of seawater (Hem 1985) to plot and interpret the chemical data. The PHREEQC software (Parkhurst and Appelo 1999) was used to determine the soluble ionic species and saturation indices (SI).

Results

Water balance

The annual rainfall records (1909–2014) suggest the occurrence of dry and wet years, also showing in the mean annual values alternating rainy and dry periods (Fig. 2a). The water balance shows a mean annual rainfall of 897 mm and an annual actual evapotranspiration that reaches 758 mm.
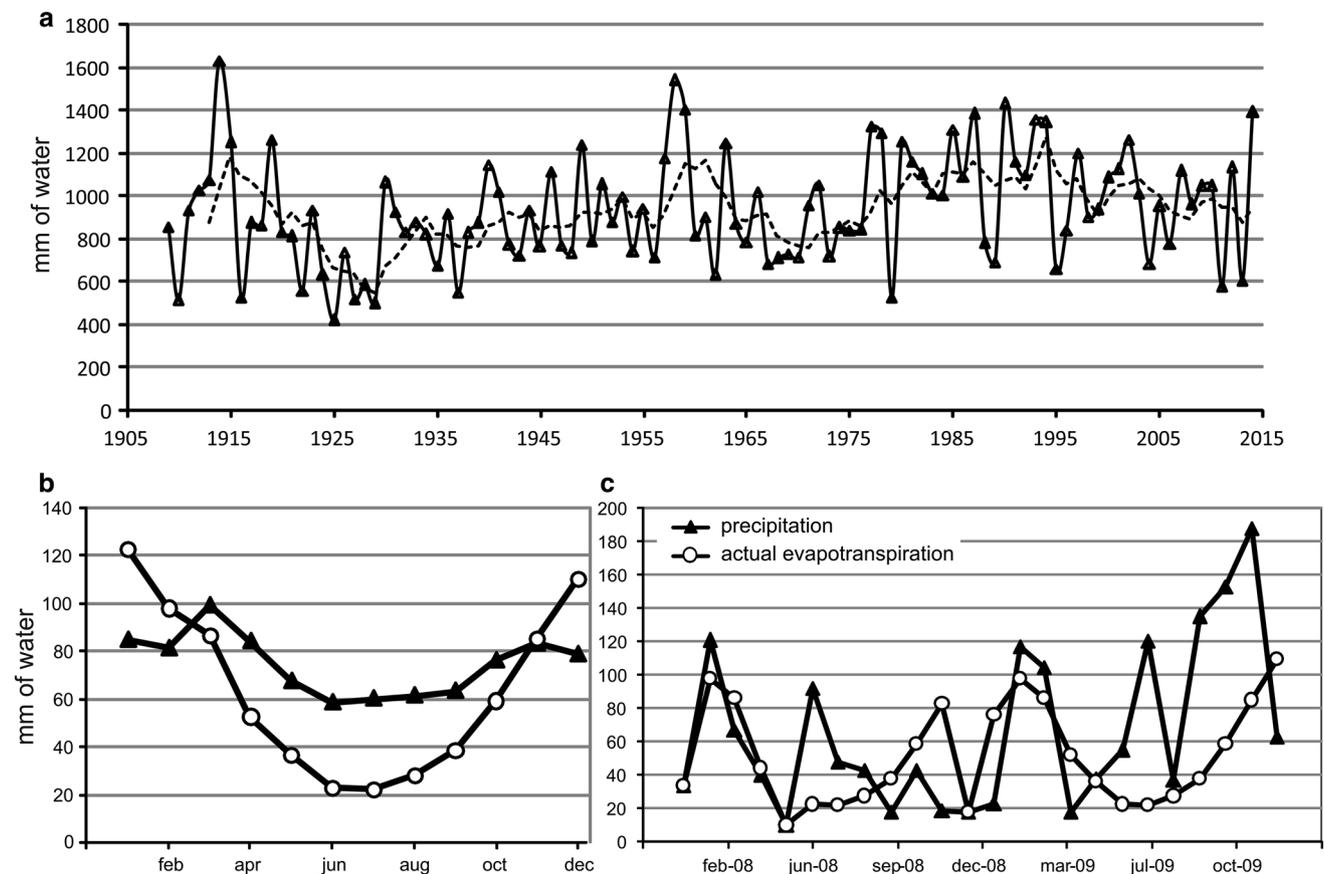
Fig. 2 a Annual precipitation for the 1909–2014 period and water balance, b for the 1909–2014 period, c for 2008 and 2009
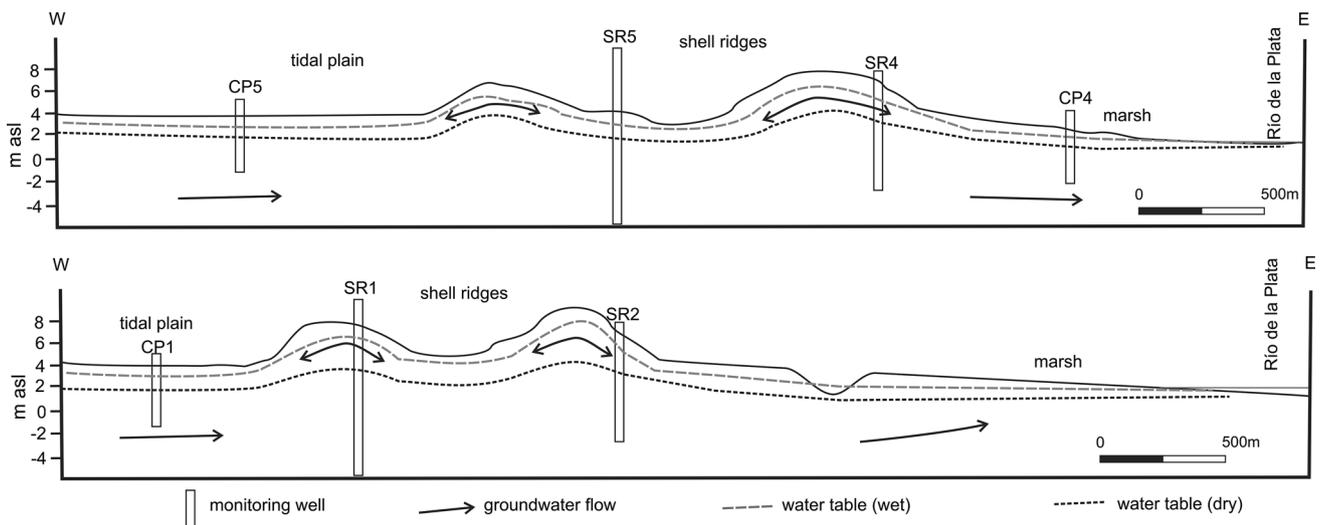
**Fig. 3** Groundwater flow cross sections for the wet and dry periods

Between the months of March and November, the precipitation is higher than the actual evapotranspiration, whereas between December and February the evapotranspiration predominates (Fig. 2b). The annual balances carried out for 2008 and 2009 (Fig. 2c) indicate that 2008 was a dry year with a precipitation of 553 mm and an actual evapotranspiration of 542 mm (i.e., 98 % of the precipitation). The water chemistry data obtained in December 2008 are representative of the end of a dry year, in which the monthly precipitation hardly ever exceeded 20 mm, and the real evapotranspiration was higher than the precipitation in the previous 6 months (Fig. 2c). On the other hand, 2009 was a wet year, with precipitation reaching 1052 mm. In that year, the actual evapotranspiration was 712 mm, with water excesses in most months (Fig. 2c). The December 2009 samples represent the end of a wet year after 6 months of water excess, with monthly precipitation in excess of 120 mm in most of those months.

Hydrochemical characteristics

Based on geological, geomorphological and hydrological characteristics, three hydrogeomorphological units can be recognized within the wetland: coastal plain groundwater (CPGW), shell-ridge groundwater (SRGW) and coastal plain surface water (CPSW).

Coastal plain groundwater (CPGW)

The coastal plain unit has low hydraulic conductivity, and the water table is shallow, between 1.30 and 2.50 m in 2008 (dry period) and between 0.10 and 0.50 m in 2009 (wet period). The regional flow discharges into the bay and locally into watercourses (Fig. 3).
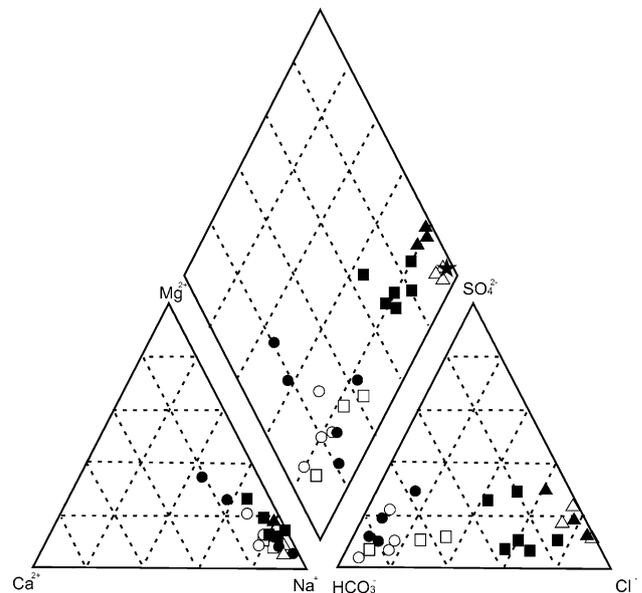
Fig. 4 Piper diagram for water sample classification. *Circles* indicate SRGW; *squares* CPGW; *triangles* CPSW (*black*: dry period; *white*: wet period). *Stars* indicate a seawater composition

CPGW is a sodium chloride type during the dry period, with salinity values ranging from 1662 to 6450 mg/L, and a sodium bicarbonate type during the wet period, with salinities between 526 and 964 mg/L (Fig. 4; Table 1). Toward the north, there is a regional decrease in salinity values. During the dry period, in the northern sector, the Cl^- content is 523 mg/L, while the Na^+ content is 286 mg/L, showing an increase toward the central sector to 1773 and 1590 mg/L, respectively. In turn, the samples collected during the wet period show a significant decrease in ion content. The high

Table 1 Major ion concentrations dissolved in surface water and groundwater (in mg/L)

Sample	TDS	pH	HCO_3^-	CO_3^{2-}	SO_4^{2-}	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
Shelly ridges										
SR1(dry)	1515	8.6	714	33	281	114	30	23	381	23
SR1(wet)	278	7.6	406	0	9	17	10	11	130	9
SR2(dry)	690	8.3	500	0	96	31	14	9	202	16
SR2(wet)	209	7.4	263	0	25	31	6	9	103	8
SR3(dry)	612	7.9	506	0	55	24	27	23	102	18
SR4(dry)	565	8.1	384	0	34	33	32	30	78	25
SR5(dry)	696	8.6	519	18	49	42	5	5	181	15
SR5(wet)	222	7.4	244	0	14	28	12	5	86	15
SR6(wet)	285	7.4	181	0	45	56	18	25	34	8
Coastal plain										
CP1(dry)	5565	7.8	1110	0	1272	1773	32	118	1590	60
CP1 (wet)	539	7.2	795	0	25	32	10	17	278	16
CP2(dry)	2975	7.8	976	0	606	773	29	69	602	65
CP3(dry)	6450	7.5	824	0	476	2727	113	106	1378	41
CP4(dry)	2220	8.1	659	0	170	844	26	30	445	12
CP4(wet)	964	7.8	275	0	35	64	11	9	126	12
CP5(dry)	1687	7.6	378	0	64	577	23	29	329	11
CP5(wet)	526	7.3	395	0	69	141	15	9	232	12
CP6(dry)	1662	7.6	506	0	76	523	38	59	286	21
Surface water										
SW1(dry)	8030	8.6	659	33	1774	2909	151	215	2230	68
SW1(wet)	3710	7.8	568	0	820	2485	16	63	2039	66
SW2(dry)	14,310	8.4	525	27	1826	6364	187	390	3930	107
SW2(wet)	6410	7.9	388	0	1118	6638	10	54	4821	78
SW3(dry)	16,055	8.0	281	0	1368	7546	211	456	4240	142
SW3(wet)	4770	7.9	478	0	1152	6182	128	28	2685	74
SW4(dry)	15,710	8.1	207	0	1294	7455	204	403	4050	144

concentrations in the Cl^-, SO_4^{2-}, Na^+ and Mg^{2+} ions, and to a lesser extent in Ca^{2+}, determine the high salinity content of the coastal plain (Table 1).

The Na^+/Cl^- ratio is close to the one of seawater during the dry period, and it tends to increase during the wet period (Fig. 5a). A similar behavior occurs in the Ca^{2+}/SO_4^{2-} ratio, but with further dispersion of the samples around the seawater ratio (Fig. 5b). Except for the case of one sample, the Ca^{2+}/HCO_3^- ratio is below 1 (Fig. 5d). In general, the samples show a slight Na^+ excess associated with Ca^{2+} and Mg^{2+} deficiencies located below the 1:1 line (Fig. 5e). The SI for halite fluctuate between −4.1 and −5.5 during the dry period and between −6.0 and −6.8 during the wet period, whereas the SI for gypsum oscillate between −2.5 and −2.7 and between −1.2 and −2.2, respectively (Fig. 6a, b). In turn, two samples from the dry period are oversaturated with calcite, with the samples from the wet period showing the most negative SI values (Fig. 6c).

Shell-ridge groundwater (SRGW)

The SRGW unit has medium to high hydraulic conductivity (20–200 m/day), and freshwater lenses occur in the saline aquifer of the coastal plain. These are preferential recharge areas where groundwater flows from the crest of the ridge to the coastal plain (Fig. 3). During the dry period sampled, the depth of the water table varied from 5 m on the crests to 3 m in the areas adjacent to the coastal plain, showing during the wet period several rises in the water table, which was located at depths of between 2 and 1 m (Fig. 3).

SRGW is a bicarbonate sodium type (Fig. 4), with a salinity content generally lower than 1000 mg/L, whose pH varies between 7.4 and 8.6 (Table 1). In dry periods, the concentration of HCO_3^- fluctuates between 384 and 714 mg/L, and of Na^+ between 78 and 381 mg/L (Table 1). The data obtained in wet periods show a decrease in content in all ions.
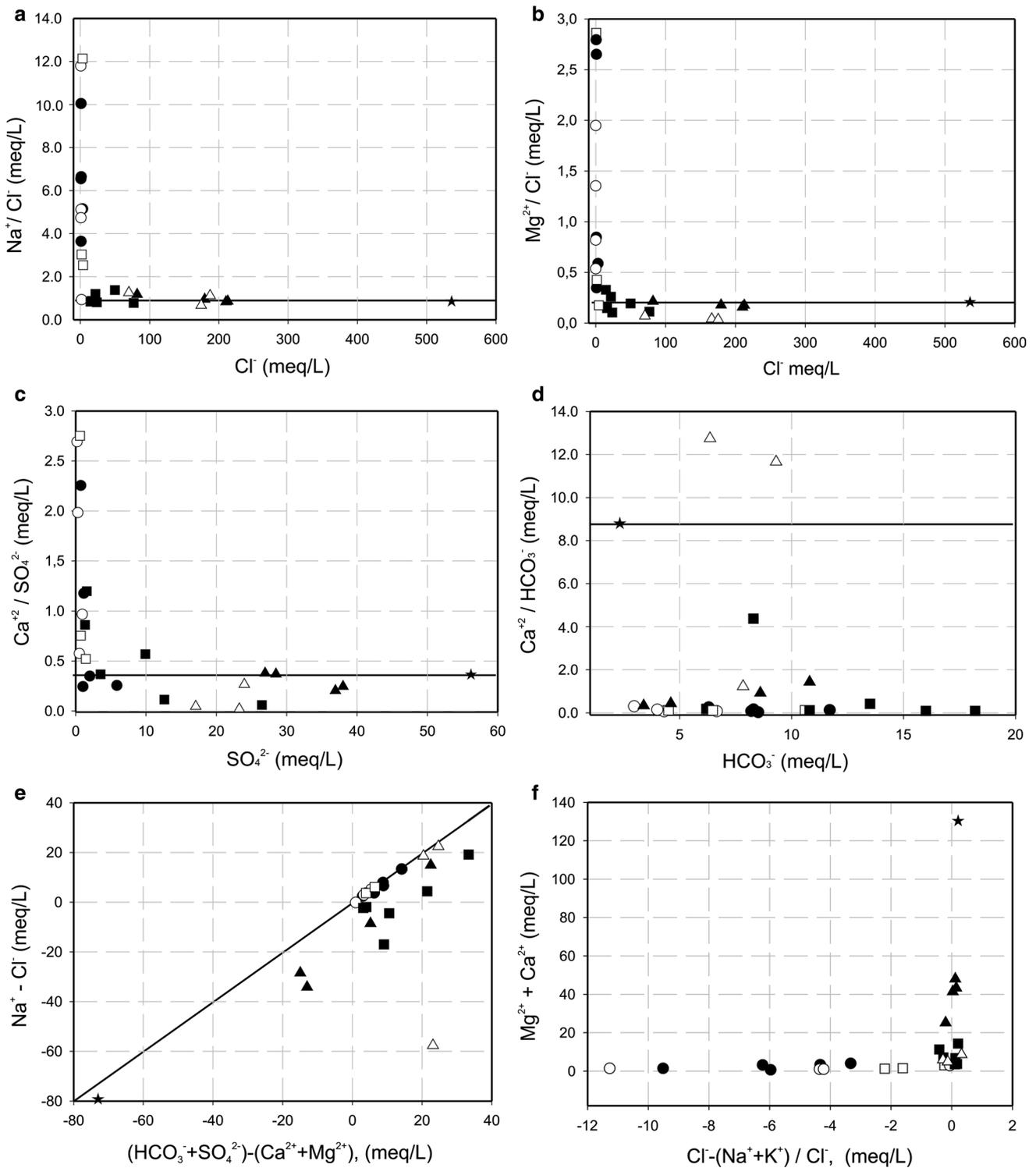
Fig. 5 Ion ratios. *Circles* indicate SRGW; *squares* CPGW; *triangles*, CPSW (*black*: dry period; *white*: wet period). *Stars* indicate a seawater composition

Both during the wet and dry periods, the Na^+/Cl^-, Ca^{2+}/SO_4^{2-} and Mg^{2+}/Cl^- ion ratios associated with the dominant ions in seawater show much higher values than those in CPGW and CPSW (Fig. 5a–c). The samples obtained in this environment have Na^+ excesses and Ca^{2+} and Mg^{2+} deficiencies in a 1:1 ratio (Fig. 5e), which are more marked
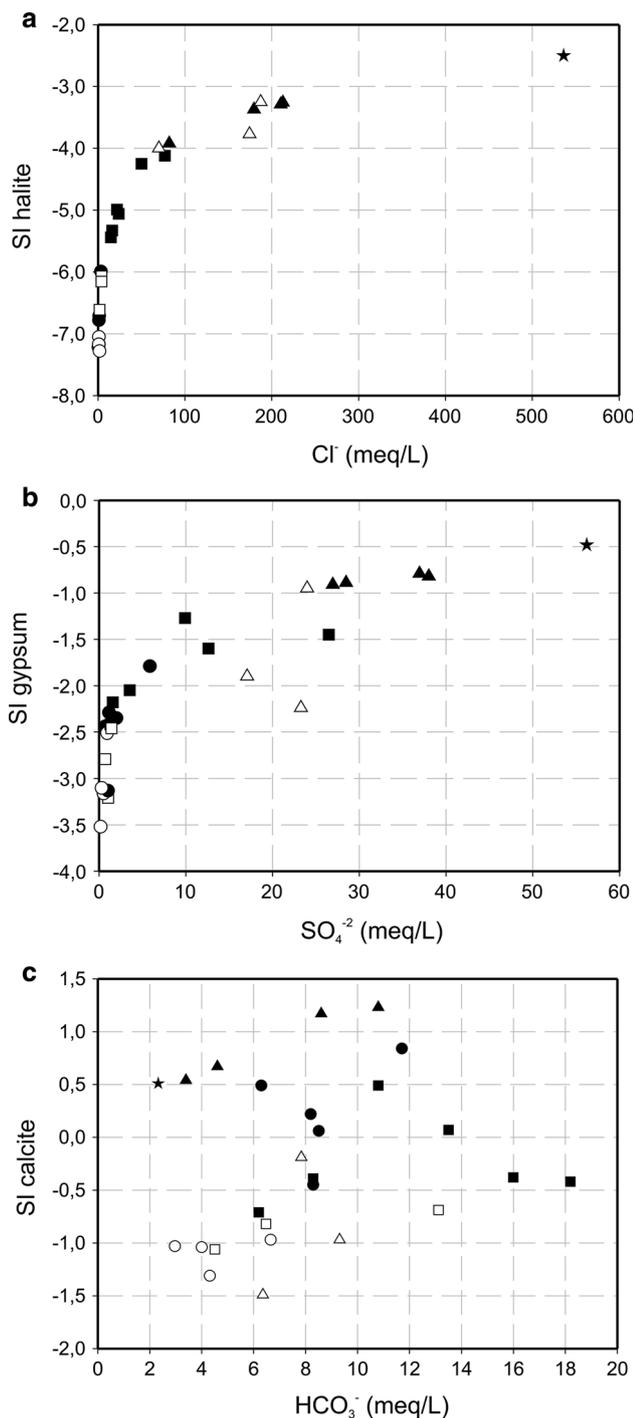
Fig. 6 Ratios between major anions and saturation indices. *Circles* indicate SRGW; *squares* CPGW; *triangles* CPSW (*black*: dry period; *white*: wet period). *Stars* indicate a seawater composition

during the dry period. This characteristic is also evident in the negative values of $Cl^- - (Na^+ + K^+)/Cl^-$, which are associated with low Ca^{2+} and Mg^{2+} contents (Fig. 5f).

The SI for halite and gypsum are undersaturated both in the dry period and in the wet period (Fig. 6a, b), showing values between −7.5 and −6.0 for halite and between −3.5

and −1.7 for gypsum. Considerable variations may be observed in the SI values for calcite (Fig. 6c), which show oversaturated values (0.1 and 0.9) during the dry period and undersaturated values (between −1.5 and −1.0) during the wet period.

Coastal plain surface water (CPSW)

CPSW is a sodium chloride type in both periods (Fig. 3) with higher salinity in the dry period. The chemical characteristics of the watercourses analyzed show intermediate ion concentrations between coastal plain groundwater and seawater (Table 1). In the dry period, the lowest salinity contents recorded occur in the Canal 15, with a value of 8030 mg/L, together with 2909 mg/L of Cl^- and 2230 mg/L of Na^+. Salinity contents in the Salado River, its relief canal and in the Samborombón River are approximately 15,000 mg/L, with Cl^- concentrations ranging from 6364 to 7546 mg/L and Na^+ concentrations from 3930 to 4240 mg/L. The samples collected in wet periods indicate a significant decrease in ion content (Table 1).

The Na^+/Cl^-, Ca^{2+}/SO_4^{2-} and Mg^{2+}/Cl^- ion ratios are similar to those of seawater, both during the wet and the dry periods, whereas the Ca^{2+}/HCO_3^- ratio during the dry period is close to 1, and during the wet period, two of the samples reach values between 11 and 13 (Fig. 5a–c). The samples obtained during the dry period show both Na^+, Ca^{2+} and Mg^{2+} excesses and deficiencies, while in those collected during the wet period only Ca^{2+} and Mg^{2+} deficiencies and Na^+ excesses are recorded (Fig. 5e). The $Cl^- - (Na^+ + K^+)/Cl^-$ values vary between −1 and 1, with the highest Ca^{2+} and Mg^{2+} contents occurring during the dry period (Fig. 5f).

The SI for halite are undersaturated and vary between −3 and −4, with no significant differences between the dry and wet periods (Fig. 6a). The SI for gypsum are also undersaturated and show less negative values (between −0.8 and −0.7) during the dry period than during the wet period (between −2.3 and −0.9) (Fig. 6b). In turn, the SI values for calcite (Fig. 6c) show oversaturated values between 0.5 and 1.3 during the dry period and undersaturated values between −1.5 and −0.1 during the wet period.

Hydrological and geochemical processes conditioning water chemistry

Processes in CPGW

The low topography of the coastal plain favors tidal inflow, which floods the more continental sectors during spring high tides and storm events. The predominance of Cl^-, SO_4^{2-}, Na^+ and Mg^{2+} ions, as well as the fact that the

values of the Na^+/Cl^- ratios are similar to the values of seawater, provide evidence that the tidal inflow has an influence on the chemistry of the coastal plain groundwater.

In the dry years, the amount of water that may be evapotranspired is similar to the annual rainfall, as observed in the water balance for 2008, in which the actual evapotranspiration represents 98 % of the precipitation. During such periods of high evapotranspiration, the coastal plain soils show desiccation cracks and salt crusts mainly composed of halite and gypsum (Carol et al. 2013). The precipitation of halite results from the total evaporation of the tidal water that fails to infiltrate and accumulates on the surface in the most depressed undrained areas. The flooding of the coastal plain during subsequent high tides or rainwater may dissolve these salts. This process would explain the high Cl^- and Na^+ concentrations with Na^+/Cl^- ratios close to 1, which mainly occur during the dry period.

In the wet periods, the precipitation is considerably higher than the evapotranspiration, as observed in the balance for 2009. The conditions favoring the formation of evaporite salts mainly occur during the summer months, when the temperature is higher and the real evapotranspiration may exceed the precipitation. On the other hand, during the rainy periods, the infiltration of rainwater causes a decrease in the concentration of all of the ions dissolved in groundwater by dilution. It should be noted that despite the low permeability of the sediments, the low topographic slope favors infiltration processes over surface runoff processes.

Carbonate concretions and shell debris are also components of the sediments of the coastal plain that may be affected by dissolution and/or precipitation processes. During the dry period, some groundwater samples are oversaturated with respect to calcite. The evaporation of tidal water before infiltrating would explain the higher SI, and it may also be the process that favors the precipitation of carbonates during the dry periods. In the rainy years, the dissolution of atmospheric $CO_{2(g)}$ during rainwater infiltration causes the dissolution of carbonates, with SI undersaturated with respect to calcite in groundwater. The excess of HCO_3^- with respect to Ca^{2+} may result from the dissolution of atmospheric $CO_{2(g)}$ or from the oxidation of organic matter, which is abundant in coastal plains and marshes. Further details on these processes of calcium carbonate dissolution/precipitation appear below when discussing SRGW, as these mineral facies are the main components of the aquifer.

Finally, the presence of elevated concentrations of SO_4^{2-} in the groundwater of the coastal plain could be due to the dissolution of gypsum that may precipitate together with halite by evaporation (Carol et al. 2009). However, there are SO_4^{2-} excesses with respect to Ca^{2+}, with a Ca^{2+}/SO_4^{2-} ratio below 1. The oxidation of sedimentary pyrite would explain these excesses (Logan and Nicholson 1998; Carol et al. 2013). Both processes would have a greater relevance during the dry period, as observed in the samples collected in 2008, which have higher SO_4^{2-} contents with respect to those from 2009 (wet period). The higher evapotranspiration favors the presence of gypsum in the sediments, and its inflow into groundwater is associated with its dissolution by the tidal flow or the rain. In turn, the lowering of the water table that occurs during the dry period causes oxidizing conditions in sectors that were previously saturated in water and under reducing conditions, therefore, allowing the oxidation of pyrite.

Processes in SRGW

The Na^+/Cl^-, Ca^{2+}/SO_4^{2-} and Mg^{2+}/Cl^- ratios, unlike CPGW and CPSW, suggest that water mixture from other environments (i.e., the coastal plain, watercourses and estuarine water) does not occur in this hydrological unit. The chemical characteristics of this unit are mainly determined by its lithological composition. Calcium carbonate is one of the main sources of ions due to the abundance of shell debris of carbonate composition.

The evolution of carbonate facies depends on the contribution of $CO_{2(g)}$ (atmospheric or derived from the decomposition of organic matter) and on the infiltration of rainwater. Rainwater reacts with $CO_{2(g)}$ to form H_2CO_3, which dissolves the carbonate facies, generating Ca^{2+} ions and HCO_3^- solution (Apelo and Postma 2005). The constant contribution of $CO_{2(g)}$ and the abundance of calcium carbonate facies enables such reactions, leading to groundwater with calcite SI above 0 (Fig. 6c). This dissolution mainly occurs during the periods of higher precipitation, in which the samples show more negative calcite SI values.

During the dry periods, the evaporation of shallow groundwater becomes relevant as it leads to an increase in salinity content. As a result, the activity of the Ca^{2+} and HCO_3^- ions reaches oversaturation values with respect to calcite, causing the precipitation of carbonates (Fig. 6c). These carbonates are usually part of the soil matrix, and their dissolution and precipitation are strongly dependent on the rainfall regime (Imbellone and Giménez 1997).

The hydrochemistry of this unit is not solely determined by this process, as it is dominated by sodium bicarbonate type water due to the fact that base exchange processes (Ca^{2+} for Na^+) occur exclusively in this unit. The Ca^{2+} that results from carbonate dissolution is exchanged by Na^+, generating sodium bicarbonate type water. Such a process is apparent in the chemical characteristics of the water with a Na^+/Cl^- ratio based on $(HCO_3^- + SO_4^{2-}) - (Ca^{2+} + Mg^{2+})$ close to 1 and negative values

of $(Cl^- - (Na^+ - K^+))/Cl^-$ and Ca^{2+}/HCO_3^- below 1 (Fig. 5d–f). The most elevated values of Na^+ excesses and Ca^{2+} and Mg^{2+} deficiencies occur during the dry periods. This could be due to the fact that, as explained above, during the dry period, calcite precipitation occurs, causing a decrease in the Ca^{2+} in solution and an increase in the proportion of the Na^+ dissolved in water.

Hydrogeochemical processes in CPSW

A large area of the plain of the Buenos Aires province drains into watercourses, which receive the contribution of the groundwater recharge of the coastal plain in the study area. Surface runoff is slow, and at high tide, water from the estuary can flow into the watercourses toward the continent up to 10 km from the shores of the bay. In the Río de la Plata estuary water, there is a salt wedge associated with the seawater from the ocean. At high tide, the salt wedge advances toward the continent and part of the estuary water may be retained in the coastal plain at low tide. As a result, in the coastal area, watercourses show highly variable hydrochemical mixing.

In dry periods, the groundwater discharge and the influence of the estuary dominate the chemical composition of CPSW. Both the surface and groundwater of the coastal plain show Na–Cl type water, as does the salt wedge in the estuary. The predominance of Cl^-, SO_4^{2-}, Na^+ and Mg^{2+} ions, as well as the values of the Na^+/Cl^- and Ca^{2+}/SO_4^{2-} ratios, are similar to seawater and CPGW, which also constitutes evidence of the influence of the estuary and groundwater discharge in the water chemistry during the dry periods. Besides, CPSW samples have SI for calcites that are oversaturated, with slightly higher values than those of CPGW and seawater.

In the wet periods, the drainage of the continental water surplus increases and, consequently, the salinity content of the surface water decreases. During such periods, the water drainage increases, causing the tidal inflow toward the continent—through the propagation of the high tide along the surface watercourses—to be reduced. Therefore, in these periods, the surface runoff of the water excess from the precipitations that fail to infiltrate and, to a lesser extent, the groundwater recharge and tidal inflow determine the chemistry of CPSW.

Conclusions

The results obtained show that the variations in rainfall regime condition the hydrological and geochemical processes that regulate the quality of surface and groundwater in the Samborombón Bay coastal wetland.

During the dry period, the evapotranspiration has the same relevance as precipitation in the annual water balance. In such conditions, it is possible for the formation of gypsum and halite to occur in the coastal plain, as a consequence of the evapotranspiration of the tidal water that floods this environment. The formation of these salts determines the chemistry of CPGW, as they are subsequently dissolved by the rainfall or high tides and enter the water table by infiltration. The contribution of sulfates due to the oxidation of sedimentary pyrite is another process occurring in CPGW, which is favored during dry periods by the lowering of the water table and the generation of oxidizing conditions. The oversaturation both in CPGW and in SRGW causes the precipitation of calcium carbonates. This process is more significant in SRGW due to the importance of the carbonate facies in this hydrogeological unit. As regards surface water, the volume of water drained is limited during the dry periods, which allows a larger tidal inflow during the high tide. The dominant processes are the tidal inflow and groundwater discharge from CPGW.

During wet periods, evapotranspiration only exceeds precipitation in the summer months, promoting only during such months the formation of gypsum and halite. In these periods, the infiltration of rainwater toward the water table predominates, leading to a decrease in the concentration of the ions dissolved by dilution. This causes the undersaturation of groundwater with respect to calcite, allowing the dissolution of the carbonate facies. As the rainfall regime increases, the volume of water drained by the rivers and canals also increases, discharging with more energy toward the bay and decreasing the tidal inflow.

The alternating dry and wet periods that characterize the Samborombón Bay wetland area cause the different hydrological and geochemical processes to act to a greater or lesser degree depending on the rainfall regime, thus causing variations in water quality.

References

Apelo C, Postma D (2005) Geochemistry, groundwater and pollution, 2nd edn. Balkema, Amsterdam

APHA American Public Health Association (1998) Standard methods for the examination of water and wastewater, 20th edn. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC

Balay MA (1961) El Río de la Plata entre la atmósfera y el mar. Publicaciones del Servicio de Hidrografía Naval H-612. Buenos Aires

Bianchi T (2006) Biogeochemistry of estuaries. Oxford University Press, Oxford

Cahoon DR, Hensel PF, Spencer T, Reed DJ, McKee KL, Saintilan N (2006) Coastal wetland vulnerability to relative sea-level rise:

wetland elevation trends and process controls. In: Wetlands and natural resource management, pp 271–292

Canevari P, Blanco DE, Bucher E, Castro GY, Davidson I (1998) Los Humedales de la Argentina. Clasificación, situación actual, conservación y legislación. Publicación N 46. Wetlands International, Buenos Aires, Argentina, p 208

Carol E, Kruse E (2012) Hydrochemical characterization of the water resources in the coastal environments of the outer Río de la Plata estuary, Argentina. J S Am Earth Sci 37:113–121

Carol E, Kruse E, Mas Pla J (2009) Hydrochemical and isotopical evidence of ground water salinization processes on the coastal plain of Samborombón Bay, Argentina. J Hydrol 365:335–345

Carol E, Kruse E, Pousa J (2010) Eco-hydrological role of deep aquifers in the Salado sedimentary basin in the Province of Buenos Aires, Argentina. Environ Earth Sci 4:749–756

Carol E, Kruse E, Vera F (2011) Formación de sulfuros en sedimentos de marismas y su relación con la presencia de sulfatos en el agua subterránea. XVIII Congreso Geológico Argentino, pp 1432–1433

Carol E, Mas Pla J, Kruse E (2013) Interaction between continental and estuarine waters in the wetlands of the northern coastal plain of Samborombón Bay, Argentina. Appl Geochem 34:152–163

Fidalgo F, Colado U, De Francesco F (1973) Sobre ingresiones marinas cuaternarias en los partidos de Castelli, Chascomús y Magdalena (Provincia de Buenos Aires). V Congreso Geológico Argentino 4:225–240

Fucks E, Schnack E, Aguirre M (2008) Reconsideración estratigráfica de las secuencias marinas Holocenas, del sector continental de la Bahía de Samborombón, Provincia de Buenos Aires. Actas de XVII Congreso Geológico Argentino, pp 1210–1211

Guerrero R, Acha E, Framiñan M, Lasta C (1997) Physical oceanography of the Río de la Plata Estuary, Argentina. Cont Shelf Res 17:727–742

Hem JD (1985) Study and interpretation of the chemical characteristics of natural water. US Geological Survey Water Supply Paper 2254

Imbellone PA, Giménez JE (1997) Micromorphology of soils in Quaternary littoral sequences. Northeastern Buenos Aires Province, Argentina. In: Shoba S, Gerasimova M, Miedema R (eds) Soil micromorphology: studies on soil diversity, diagnostic and dynamics. Moscow-Wageningen, pp 93–105

Logan W, Nicholson R (1998) Origin of dissolved groundwater sulphate in a coastal plain sediments of the Río de la Plata, Argentina. Aquatic Geochem 3:305–328

Manda AK, Giuliano AS, Allen TR (2014) Influence of artificial channels on the source and extent of saline water intrusion in the wind tide dominated wetlands of the southern Albemarle estuarine system (USA). Environ Earth Sci 71:4409–4419

Marimuthu S, Reynolds D, Le Gal La Salle C (2005) A field study of hydraulic, geochemical and stable isotope relationships in a coastal wetland system. J Hydrol 315:93–116

Nasir UP, Harikumar PS (2012) Hydrochemical and isotopic investigation of a tropical wetland system in the Indian subcontinent. Environ Earth Sci 66:111–119

Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC (Version 2). A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: US Geological Survey Water-Resources Investigations Report 99-4259

Patra S, Liu CQ, Wang FS, Li SL, Wang BL (2012) Behavior of major and minor elements in a temperate river estuary to the coastal sea. Int J Environ Sci Technol 9:647–654

Sola F, Vallejos A, Moreno L, López Geta JA, Pulido Bosch A (2012) Identification of hydrogeochemical process linked to marine intrusion induced by pumping of a semiconfined Mediterranean coastal aquifer. Int J Environ Sci Technol. doi:10.1007/s13762-012-0087-x

Terzic J, Peh Z, Markovic T (2010) Hydrochemical properties of transition zone between fresh groundwater and seawater in karst environment of the Adriatic islands, Croatia. Environ Earth Sci 59:1629–1642

Thornthwaite CW, Mather JR (1957) Instructions and tables for computing potential evapotranspiration and the water balance. Publ Climatol 10:185–311

Violante R, Parker G, Cavallotto J (2001) Evolución de las llanuras costeras del este bonaerense entre la bahía de Samborombón y la laguna de Mar Chiquita durante el Holoceno. Revista de la Asociación Geológica Argentina 56:51–66