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Hydrochemical characterization of the water resources in the coastal environments of the outer Río de la Plata estuary, Argentina

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ABSTRACT

Hydrogeochemical processes affecting the chemical composition of groundwater and surface water in the coastal areas of the central and northern sectors of the outer Río de la Plata estuary in Argentina are evaluated. Results indicate hydrochemical differences between the three hydrological units analyzed. In shell ridges, groundwater is a low-salinity sodium bicarbonate type with a predominance of $CO_{2(g)}$ dissolution, carbonate dissolution and ion exchange. In the coastal plain, groundwater is a saline sodium chloride type and its chemical characteristics are related to the contribution of water from the estuary, the dissolution of gypsum and halite, and the oxidation of pyrite. Surface waters are a sodium chloride type and their composition shows the incidence of tidal water flowing into the continent. In this area a wetland occurs and it is regarded as a natural reserve that depends to a large extent on its hydrological characteristics. Knowledge of the processes regulating the hydrochemistry would constitute an essential tool in the management and preservation of the environmental characteristics of this system.

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1. Introduction

Bays and estuaries are regions in which large changes in water chemistry, sediment composition and biological characteristics may occur on a small spatial and temporal scale (Bianchi, 2006). The coastal areas associated to these environments are characterized by a complex hydrological dynamics with a strong interaction between groundwater, surface water and estuarine water. Ion ratios in hydrogeochemical tests make it possible to determine the water–sediment interaction (dissolution–precipitation, oxidation–reduction, ion exchange), to establish possible water mixtures (seawater intrusion, contribution from different aquifers), to define sources and contamination processes, etc. The study of the ion ratios also constitutes an invaluable tool to explain the geochemical processes that determine water composition in coastal hydrological environments (Giménez and Morell, 1997; Jorgensen, 2002; Marimuthu et al., 2005; De Montety et al., 2008; Silva-Filho et al., 2009).

The Río de la Plata estuary is a relevant hydrological system for the socioeconomic and ecological development of the coast of the Buenos Aires province, Argentina, and of Uruguay. Geographically it is subdivided into three zones: the upper Río de la Plata, from its source to the imaginary line that connects Buenos Aires and Colonia; the middle Río de la Plata up to the line connecting Punta Piedras and Punta Brava; and the outer Río de la Plata up to the line joining Punta Rasa and Punta del Este (Fig. 1).

The Río de la Plata is a salt-wedge estuary in which the dynamics are determined by the contribution of its tributaries and by the influence of the oceanic tidal wave (Balay, 1961). Water salinity content in the different sectors of the estuary reflects the predominance of either one of the contributing sources.

On the Argentinian margin of the outer estuary, the Samborombón Bay wetland is located, and in 1997 it was appointed as a Ramsar site. This wetland is an area where migratory birds feed, rest and breed, as well as a reserve for species in danger of extinction (*Ozotoceros bezoarticus celer*). In the bay coast, dense populations of crabs give the intertidal plain landscape a particular physiognomy locally known as *cangrejales* (*i.e.,* a land filled with crabs; César et al., 2005). Some of the plant species of the wetland, in the intertidal zone, are *Spartina*, *Salicornia*, and *Zizaniopsis*, whereas in elevated areas with well-drained soils (*i.e.,* the shell ridges and sandy layers) arboreal specimens of *Celtis tala* are the most typical. This vegetation contributes to the primary productivity of the region, provides nesting sites for different bird taxa, produces detritus which provides organic matter to the coastal substratum, and is the basis of the trophic webs in the region

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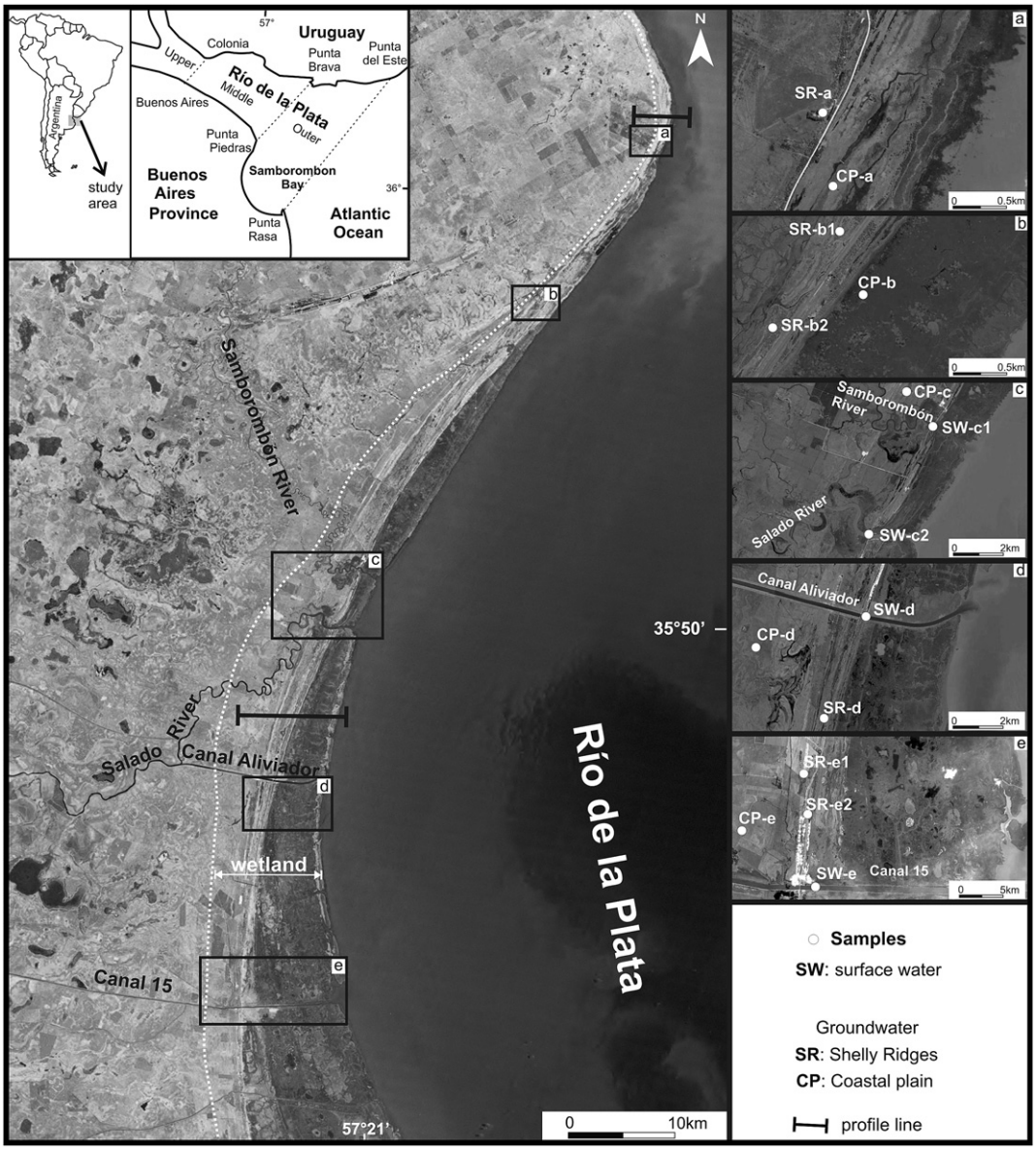

Fig. 1. Location of the study area, regional geology and location of the sampling points. The Samborombón bay wetland extends between the coastline and the white dashed line.

(Canevari et al., 1998). The wetland ecosystems have a strong hydrological dependence, with the hydrochemical characteristics being a determining factor in species distribution.

Increasing human activities (*e.g.,* cattle-raising, aggregate and shell extraction, construction of drainage canals, roads and highways) have not only affected many coastal ecosystems in the world, but they have also given rise to conflicts with respect to the available freshwater resources. The case of the Samborombón Bay wetland lies within this problematic frame to such extent as to cause some concern about its productivity and future evolution as an ecosystem.

On the Argentinian coast, the hydrological environments in the outer estuary area have not been studied in depth from a hydrogeochemical point of view, there being background data only for the southern sector of the bay (Carol et al., 2008, 2009).

The objective of this work is to evaluate the hydrological and geochemical processes that affect the chemical composition of groundwater and surface water in the coastal areas of the outer Río de la Plata estuary – specifically in its central and northern sectors – in Argentina.

Such an evaluation of the hydrological and geochemical processes is fundamental in order to develop guidelines for the sustainable management of the natural resources in the region and, in turn, the methodology and the results may be applied worldwide to other coastal areas with similar characteristics.

2. Study area

2.1. Geology and geomorphology

The outer Río de la Plata estuary comprises, on its Argentinian margin, a shoreline of approximately 180 km extending from Punta Piedras to Punta Rasa. The study area comprises an extensive coastal plain associated with shell ridges (Fig. 1).

The geological and geomorphological configuration of the area analyzed developed during the Quaternary as a consequence of successive shoreline displacements due to sea level oscillations (Violante et al., 2001). Quaternary sediments in the coastal areas of the bay correspond to a coastal plain environment with high- and low-energy deposits. The low-energy deposits are constituted by

clayey to clayey–sandy sediments. The high-energy deposits are composed of loose debris of marine shells alternating in patches with layers of sand and clay, forming raised ridges running parallel to the coastline (Fucks et al., 2010, Fig. 2). Higher shell ridges – with heights of 14 m asl – occur in the northern sector of the bay, where the tidal plain is poorly developed. The central sector is a depressed area with heights generally below 5 m asl and where the average height of the shell ridges is 7 m asl (Fig. 2).

2.2. Hydrological conditions

The climate in the region is humid temperate. The average rainfall for the 1889–2009 period is 896 mm/year, with extreme values of 1622 and 373 mm/year (Fig. 3). The annual variations in rainfall determine the existence of dry and wet periods. The mean monthly values for the same period show that the wettest month is March and the driest is June (Fig. 3). Water balances carried out in the region, considering rainfall variations, show evapotranspiration values of 553 mm/year for a dry year and 575 mm/year for a wet year (Deluchi et al., 2006).

The Río de la Plata estuary has a microtidal regime with semi-diurnal oscillations and a tidal wave range below 2 m. At high tide, seawater enters the estuary as a salt-wedge. In the upper and middle Río de la Plata, average salinity values (between 0.2 and 2 g/L) are typical of fluvial systems; whereas in the outer estuary average salinity indicates the influence of seawater. In the Punta Piedras area, average salinities are close to 3 g/L, while towards the south in Punta Rasa they reach values close to 20 g/L (Guerrero et al., 1997).

The main watercourses that flow into the area are the Samborombón River and the Salado River. Both of these courses drain a vast plain region of the Buenos Aires province (Fig. 1). Downstream, the slight slope of the area (10^{-4}) makes the natural drainage towards the bay difficult, as it is periodically hindered by tidal inflow. At low tide, the rivers and canals discharge towards the bay, whereas at high tide freshwater flows in from the estuary, penetrating up to 10 km from the coastline at high tide. In order to enable drainage, in the early 20th century numerous canals were built, the most relevant being the Salado River, the Canal Aliviador and the Canal 15 (Fig. 1).

According to their geological and geomorphological characteristics, shallow aquifers are grouped into two hydrological units: coastal plains and shell ridges (Sala et al., 1978). The coastal plain is a low hydraulic conductivity unit which contains saline groundwater. The water table is at a shallow depth and the regional flow is towards the bay, discharging locally into ponds and watercourses. Shell ridges constitute a medium to high hydraulic conductivity unit, in which freshwater lenses are formed on the saline aquifer of the coastal plain. They are preferential recharge areas with groundwater local flow from the crest of the ridge towards the coastal plain (Fig. 2). In the northern sector, the mean position of the water table is 11 m asl in the highest shell ridges and 1.75 m asl in the coastal plain, with regional gradients on the order of 0.01. In the central sector, the average height of the water table is approximately 5.5 m asl in the shell ridges and 1.25 m asl in the coastal plain, with a regional gradient within the coastal plain below 0.001 (Sala et al., 1978, Fig. 2).

3. Methodology

The hydrogeological and geomorphological characteristics of the region were studied by means of the gathering of background data, field surveys, and the analysis of topographic maps and satellite images.

A monitoring network at a regional level was created, from where samples of groundwater and surface water of the main watercourses and canals were obtained (Fig. 1). The groundwater samples were extracted from monitoring wells with an average depth of 10 m, which were set up for this study in the shell ridges and the coastal plain. In order to collect the samples, the wells were

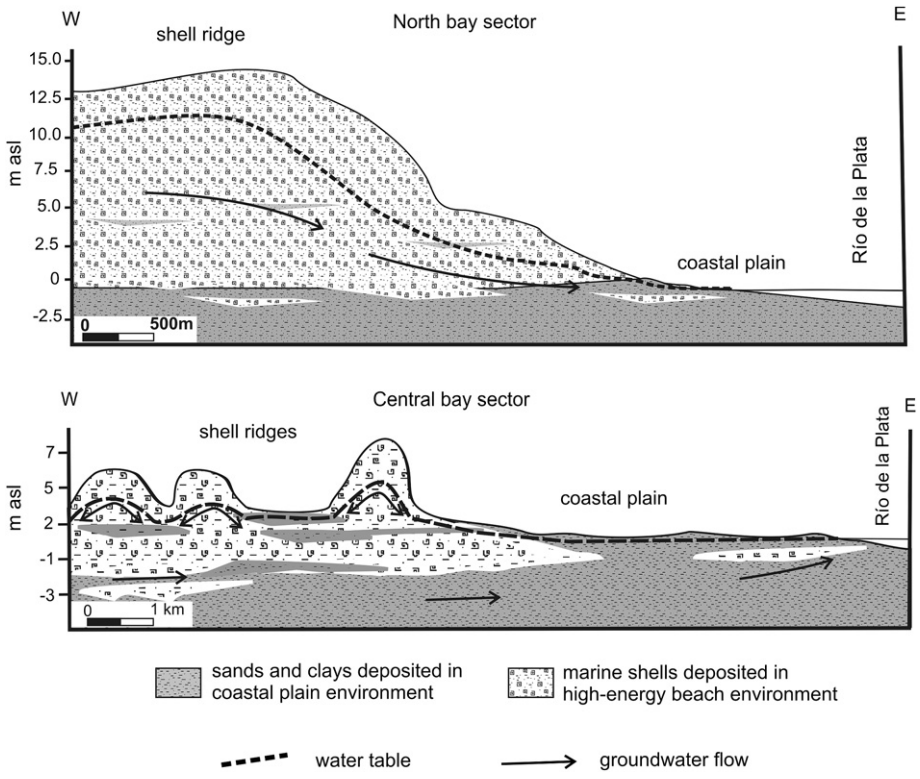

Fig. 2. Geological cross-section and hydrodynamic behaviour of the hydrological units.

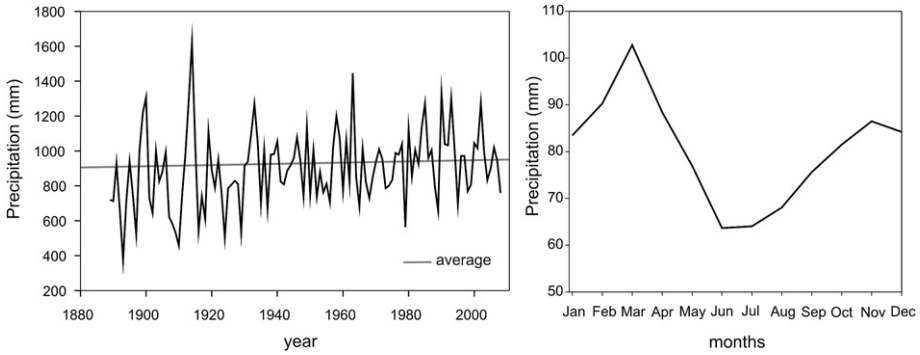

Fig. 3. Mean annual and monthly precipitations (1889–2009 period).

previously purged, pumping at least three times the volume contained in the well casing. The surface water samples were collected at low tide and they represent an integration of the ion content of the whole water column.

The data analyzed correspond to the sampling collected in August 2008 in low tide conditions. In the water samples, pH, electrical conductivity, calcium, magnesium, sodium, potassium, chloride, sulphate, carbonate and bicarbonate were measured. Chemical analyses of the major elements were conducted in keeping with the methods at the Laboratorio de Ingeniería Sanitaria, Facultad de Ingeniería, Universidad Nacional de La Plata. Sample collection, preservation, and chemical analysis of the water samples were carried out in accordance with the standard methods proposed by the American Public Health Association (APHA, 1998). Sodium (Na^+) and potassium (K^+) were determined by flame photometry. Hardness as calcium carbonate ($CaCO_3$), calcium (Ca^{2+}), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and chloride (Cl^-) were determined by volumetric methods. Magnesium (Mg^{2+}) was calculated on the basis of data on calcium and total hardness. Sulphate (SO_4^{2-}) was measured by nephelometry and the amount of total dissolved solids (TDS) was assessed by gravimetry.

The analytical error in 80% of the samples was below 10%. Electrical conductivity and pH were determined in the field immediately after the sampling by means of portable equipment.

The interpretation of the chemical data was carried out on the basis of diagrams for water classification and representation of ion ratios. The determination of water-soluble ionic species and saturation indices (SI) was conducted using the PHREEQC software (Parkhurst and Appelo, 1999).

In order to analyze tidal influence, salinity measurements were carried out in the water columns of the rivers, canals and groundwater every 0.50 m deep with a Solinst TLC manual level measurement device. Water table and water level measurements were carried out to define groundwater flow and the surface water–groundwater relationship.

4. Results

Hydrochemical characteristics provide evidence for the differentiation between the three hydrological units: groundwater of the shell ridges and coastal plain, and surface waters.

4.1. Shell ridges

The shell ridges constitute recharge areas where rainfall accumulates, forming freshwater lenses over the coastal plain with saline groundwater (Fig. 2). In these environments the lithological (high hydraulic conductivity) and morphological characteristics, as well as the lack of surface runoff, favour the infiltration of rainfall excess. The water is a bicarbonate sodium type, with a pH between 7.9 and 8.6 (Fig. 4). Salinity content is usually below 1000 mg/L; the concentration of HCO_3^- fluctuates between 384 and 714 mg/L, and of Na^+ between 78 and 381 mg/L (Table 1).

The ion ratios vary between 3.64 and 10.05 for Na^+/Cl^-, between 0.35 and 2.79 for Mg^{2+}/Cl^-, between 0.24 and 2.25 for Ca^{2+}/SO_4^{2-} and between 0.03 and 0.25 for Ca^{2+}/HCO_3^-, in every case departing from the results of the samples of the coastal plain and surface water (Fig. 5a to d). One of the characteristics of the shell ridges is that $Na^+ - Cl^-$ as a function of $(HCO_3^- + SO_4^{2-}) - (Ca^{2+} + Mg^{2+})$ has a 1:1 ratio, displaying a correlation coefficient of 0.98 (Fig. 5e). This is evidence that Na^+ excess is stoichiometrically related to the Ca^{2+} and Mg^{2+} deficiencies, making it possible to identify ion exchange processes of the Na^+/Ca^{2+} and Na^+/Mg^{2+} type. The negative values of $(Cl^- - (Na^+ + K^+))/Cl^-$, associated to low values of $Ca^{2+} + Mg^{2+}$, support the idea of ion exchange taking place (Fig. 5f).

The SI with respect to halite and gypsum are negative, whereas in all samples but one the SI with respect to calcite are positive (Fig. 6). In turn, the Gibbs (1970) diagrams show ion relation values between 0.68 and 0.97 for $Na^+/(Na^+ + Ca^{2+})$ and between 0.07 and 0.21 for $Cl^-/(Cl^- + HCO_3^-)$ (Fig. 7).

Salinity measurements carried out during a tidal period in the water column every 0.50 m do not show variations at high tide.

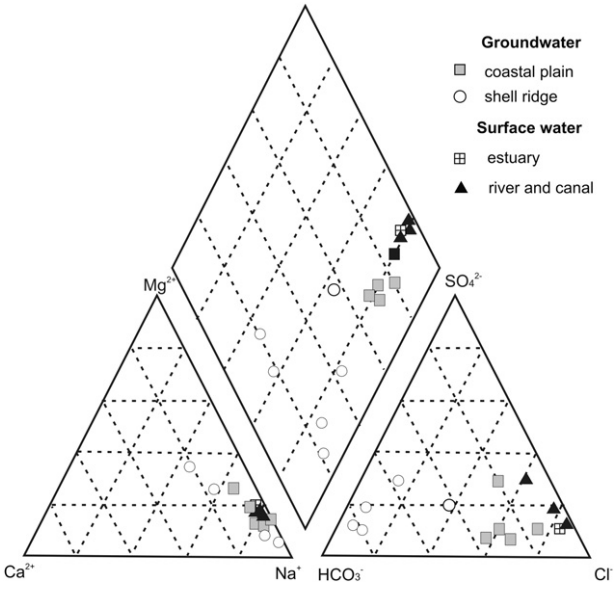

Fig. 4. Piper diagram for water sample classification.

Table 1
Hydrochemical data from 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	SR-a	1662	7.6	506	0	76	523	38	59	286	21
	SR-b1	696	8.6	519	18	49	42	5	5	181	15
	SR-b2	565	8.1	384	0	34	33	32	30	78	25
	SR-d	612	7.9	506	0	55	24	27	23	102	18
	SR-e1	690	8.3	500	0	96	31	14	9	202	16
	SR-e2	1515	8.6	714	33	281	114	30	23	381	23
Coastal plain	CP-a	1687	7.6	378	0	64	577	23	29	429	11
	CP-b	2220	8.1	659	0	170	844	26	30	645	12
	CP-c	6450	7.5	824	0	476	2727	113	106	1478	41
	CP-d	2975	7.8	976	0	606	773	29	69	802	65
	CP-e	5565	7.8	1110	0	1272	1773	32	118	1590	60
Surface water	SW-c1	15,710	8.1	207	0	1294	7455	204	403	4050	144
	SW-c2	16,055	8.0	281	0	1368	7546	211	456	4240	142
	SW-e	8030	8.6	659	33	1774	2909	151	215	2230	68
	SW-d	14,310	8.4	525	27	1826	6364	187	390	3930	107
	Estuary	14,745	7.8	272	0	1184	7273	222	432	4100	89
Surface water mix	Sea	–	–	142	0	2700	19,000	410	1350	10,500	390
	Salado	–	–	385	11	378	742	105	181	468	22

4.2. Coastal plain

The coastal plain is an area with a limited height in which the phreatic aquifer receives inflow from precipitations, the discharge of the regional and local flow from the shell ridges, and in the coastal area it also receives inflow from the estuary at high tide. The discharge of the groundwater flow in this environment is local towards the surface watercourses and regional towards the bay (Fig. 2).

In the coastal plain, water is sodium chloride type (Fig. 4), with a pH close to 7.7 and salinities between 1662 and 6450 mg/L; a regional tendency to the decrease of salinity towards the north can be observed (Table 1). In the northern sector, the Cl^- content is of 523 mg/L, and the Na^+ content of 286 mg/L, increasing towards the central sector to 1773 mg/L and 1590 mg/L respectively.

The Na^+/Cl^- and Mg^{2+}/Cl^- ratios do not vary much and are similar to those of the surface water and the estuary, with values ranging between 0.84 and 1.38, and between 0.10 and 0.33 respectively (Fig. 5a and b). In turn, Ca^{2+}/SO_4^{2-} varies between 0.06 and 1.19, Ca^{2+}/HCO_3^- between 0.09 and 0.42 (Fig. 5c and d) and the exchange relationships $(Na^+ - Cl^-)$ as a function of $(HCO_3^- + SO_4^{2-}) - (Ca^{2+} + Mg^{2+})$ do not show a correlation, and the $(Cl^- - (Na^+ + K^+))/Cl^-$ values are close to zero (Fig. 5e and f).

The SI are undersaturated with respect to halite and gypsum, whereas with respect to calcite both oversaturated and undersaturated values were observed (Fig. 6). The Gibbs diagrams show ion relation values between 0.86 and 0.97 for $Na^+/(Na^+ + Ca^{2+})$ and between 0.57 and 0.85 for $Cl^-/(Cl^- + HCO_3^-)$ (Fig. 7).

Salinity measurements carried out in the water column every 0.50 m in different sectors of the coastal plain show that in the littoral wetland areas and those adjacent to the rivers and canals water salinity varies at high tide, with samples in depth having a higher saline content than those collected on the surface.

4.3. Surface water

Estuary water is of the sodium chloride type (Fig. 4) with Na^+/Cl^-, Mg^{2+}/Cl^- and Ca^{2+}/SO_4^{2-} ion relations similar to those in seawater, but with lower ion concentrations (Table 1, Fig. 5).

Watercourses drain a vast surface of the plain of the Buenos Aires province and in the study area they receive the contribution of the groundwater recharge of the coastal plain. Runoff is slow, and at high tide estuarine water can flow into the watercourses towards the continent up to 10 km from the bay shoreline. Due to these characteristics, watercourses in the coastal area are zones of highly variable hydrochemical mixing.

Watercourses and canals are characterized by a sodium chloride type water (Fig. 4), with a pH fluctuating between 8.0 and 8.6. The lowest salinity contents are recorded in the Canal 15, with values of 8030 mg/L, associated to 2909 mg/L of Cl^- and 2230 mg/L of Na^+. In the Salado River, the Canal Aliviador and in the Samborombón River the salinity contents are close to 15,000 mg/L, with Cl^- concentrations of between 6364 and 7546 mg/L and Na^+ concentrations between 3930 and 4240 mg/L. Salinity is in every case considerably superior to the one in groundwater (Table 1, Fig. 5).

The ion relations, especially those involving the most conservative ions, show similar values to those in the estuary, with Na^+/Cl^- varying between 0.84 and 1.38, Mg^{2+}/Cl^- between 0.10 and 0.33, Ca^{2+}/SO_4^{2-} between 0.06 and 1.19, and Ca^{2+}/HCO_3^- between 0.09 and 0.42 (Fig. 5a–d).

The mixture of seawater with water from the Salado River, which runs in the sector adjacent to the study area and has no tidal influence, shows that in the study area the surface water of the Salado River and its canals has an ionic composition with 40–50% of seawater. These percentages derive from the calculations concerning the relationships involving Cl^-, as it is the most conservative ion out of the ones analyzed in the system. However, similar values can be observed in the relationships involving SO_4^{2-}.

Salinity measurements carried out in the water column every 0.50 m in the rivers and canals show that water salinity varies at high tide, with samples in depth having a higher saline content than those collected on the surface, suggesting the presence of a salt-wedge.

The tidal influence in the chemical composition of water can also be observed in the Gibbs diagrams, in which the $Na^+/(Na^+ + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ ratios observed are similar to those of seawater, but with lower TDS contents (Fig. 7).

The SI for halite and gypsum are below 1, whereas all samples show oversaturated values with respect to calcite (Fig. 6).

5. Discussion

The shell ridges are environments in which the lens-shaped groundwater accumulated over the coastal plain is not affected by the tidal hydrology of the estuary. They only receive water inflow from precipitations and their chemical characteristics depend on the interaction of water and the sediments during infiltration and groundwater runoff. Abundance of shell debris of

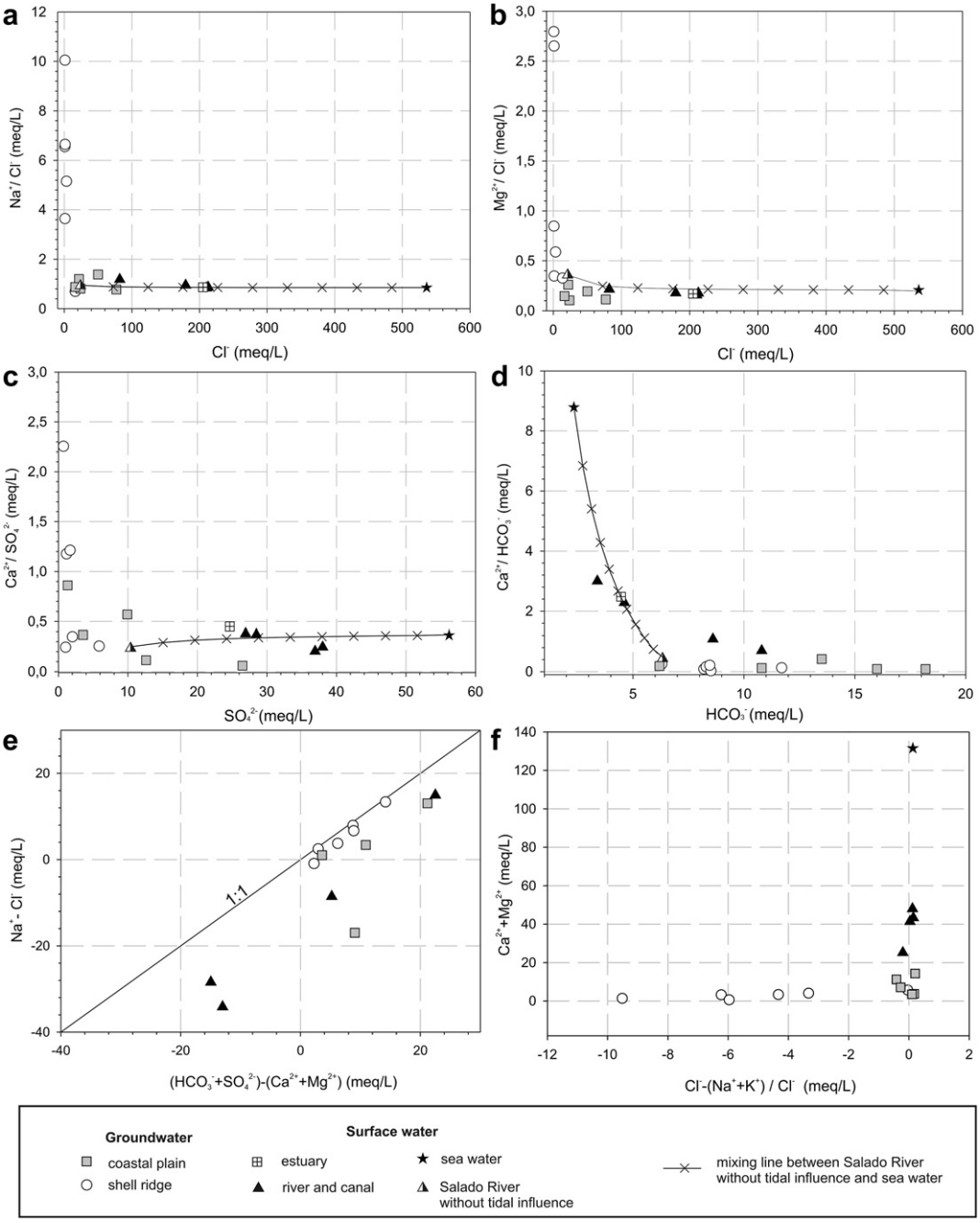

Fig. 5. Ratios between major ions.

carbonate composition determines that calcium carbonate facies be one of the main sources of ions. The evolution of carbonate facies is subject to the contribution of $CO_{2(g)}$. Rainwater dissolves atmospheric $CO_{2(g)}$ and as it infiltrates the soil it incorporates the $CO_{2(g)}$ which is trapped in the pore spaces, mainly in the areas with root growth and the presence of decomposing organic matter. The $CO_{2(g)}$ reacts with the water to form H_2CO_3, which first dissociates into HCO_3^- and H^+ ions, and then HCO_3^- into $CO_3^{2-} + H^+$, with HCO_3^- being the dominant species in the pH values ranging from 6.5 to 10 (Appelo and Postma, 2005). The protons released are consumed by carbonate dissolution ($HCO_3^- + H^+ + CaCO_3 \leftrightarrow Ca^{2+} + 2HCO_3^-$). In the unsaturated zone, which is an open system with respect to $CO_{2(g)}$, the protons consumed in the carbonate dissolution are regenerated due to the dissolution of the $CO_{2(g)}$ available in the sediment pores. When the infiltrating water enters the saturated zone, which is a closed system with respect to $CO_{2(g)}$, the protons consumed cannot be regenerated, as in this area there is no $CO_{2(g)}$ available in the system.

The constant contribution of $CO_{2(g)}$ and the abundance of calcium carbonate facies enables these reactions, giving rise to groundwater with calcite SI above 0.

This is not the only process, however, that determines the hydrochemistry of the shell ridges, since it is dominated by a sodium bicarbonate type water. This is so due to ion exchange processes (Ca^{2+} for Na^+) which take place exclusively in this unit. Sodium bicarbonate water is generated by the fact that the Ca^{2+}

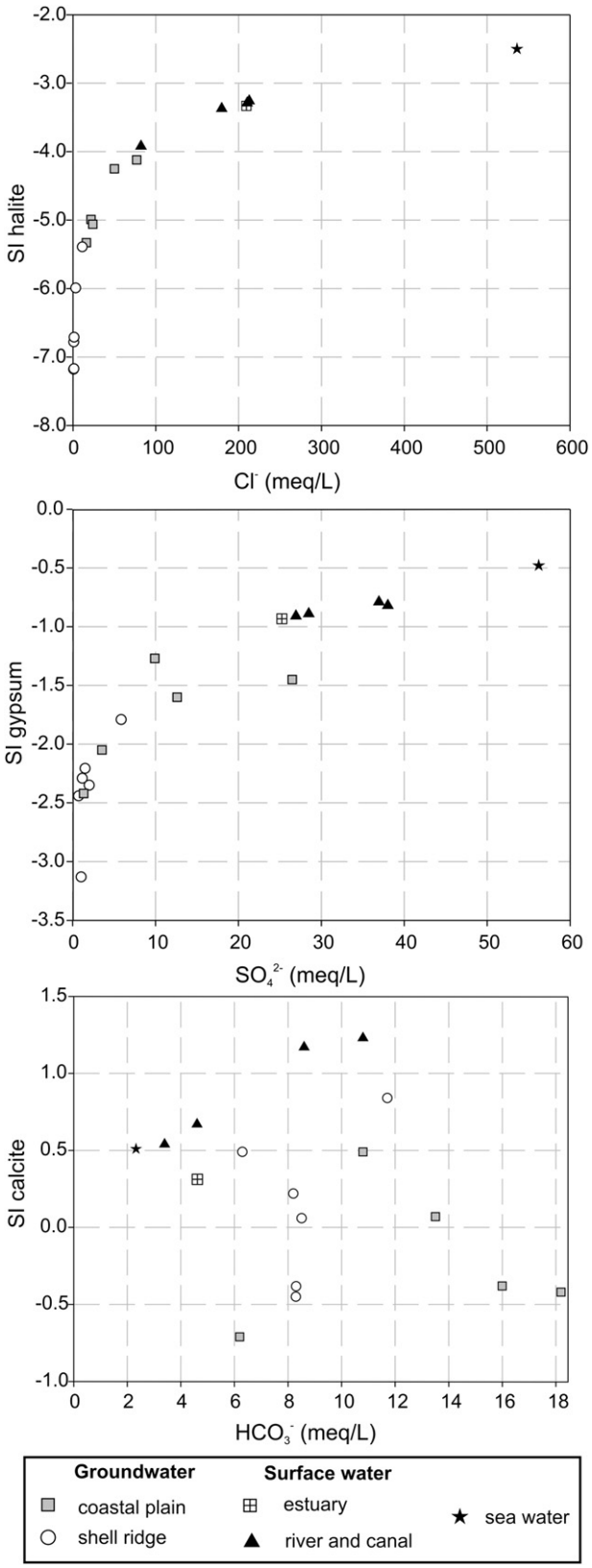

Fig. 6. Saturation indices.

arising from carbonate dissolution is exchanged by Na^+. This process is evident 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, negative values of $(Cl^- - (Na^+ + K^+))/Cl^-$, and Ca^{2+}/HCO_3^- below 1.

The sequence of the processes mentioned above begins during the deposition of the shell ridges due to marine influence. The seawater in which the Na^+ and Cl^- ions predominate is caught in the pore spaces. Under these conditions, the Na^+ which is in excess with respect to the other cations is preferably absorbed by the surface of the clayey layer occurring in the ridges. Due to the geological evolution, the sea level descended and these environments remained out of the tidal cycle and formed aquifers recharged by precipitations. The Cl^- is washed away, whereas the Na^+ remains adsorbed in the clayey layer of the aquifer. As rainwater infiltrates, it reacts to the $CO_{2(g)}$, diluting the shells and carbonate concretions and originating Ca^{2+} and HCO_3^- ions. Then the Ca^{2+} in solution is exchanged by the Na^+ adsorbed, modifying the water composition to $Na–HCO_3$ facies.

The shell ridges store freshwater in the shape of a lens. The centre of the lens is the groundwater divide, where the largest thickness of freshwater can be found. Towards the edges the freshwater thickness decreases and, in the sectors adjacent to the plain, the saline content in the water tends to increase. This can be observed in the TDS content of the samples analyzed, in which those collected in the edges of the ridges (SR-a and SR-e2) have higher TDS values than in the centre (SR-b1, SR-b2, SR-d and SR-e1).

In the coastal plain, the predominance of ions Cl^-, SO_4^{2-}, Na^+, Mg^{2+}, the values of Na^+/Cl^-, Ca^{2+}/SO_4^{2-} and Mg^{2+}/Cl^- ratios similar to the ones of estuary water and seawater, and the Gibbs diagrams provide evidence that the flooding of the coastal plain at storm high tide with estuarine water is the main process that determines the chemical characteristics observed in groundwater in this unit. The variations in salinity recorded at high tide also suggest water inflow from the estuary towards the aquifer at high tide in the areas closest to the littoral. In these areas the salt-wedge differentiation in salinity which occurs in the estuary can also be observed.

To a lesser extent, the contributions of Cl^-, Na^+, SO_4^{2-} and Ca^{2+} derive from the dissolution of halite and gypsum. These minerals are deposited superficially on the soils of the coastal plain as crusts, due to the evaporation of estuary water which floods the depressed areas. Occurrence of Ca^{2+}/SO_4^{2-} values below 1 in most samples would indicate SO_4^{2-} contribution from another source. Coastal plains and marshes usually present iron sulphide (pyrite) among the mineral components of their sediments (Borrego et al., 1992; Otero and Macías, 2002; Morse et al., 2007; Pires and Lacerda, 2008). Oxidation of these sulphides contributes to the increase in SO_4^{2-} concentration, as can be observed in other coastal plain areas (Logan and Nicholson, 1998; Brown et al., 2000).

As for the calcium carbonate facies, most samples have negative calcite SI and a Ca^{2+}/HCO_3^- ratio below 1. Excess of HCO_3^- with respect to Ca^{2+} may arise from the dissolution of $CO_{2(g)}$ from the atmosphere or deriving from the oxidation of organic matter, which is an abundant component in coastal plains and marshes.

Within the study area, the rivers and canals have a strong tidal influence, showing similar compositions to the ones in the estuary, where the average ion content has a composition comprising between a 40 and 50% mixture with seawater. The salinity values recorded in the water column at high tide show that the inflow occurs as a salt-wedge, as it does in the estuary.

The interrelationship between the groundwater of the coastal plain and the surface water of the rivers, canals and the estuary regulates the saline flows. Such an interrelationship is a conditioning factor for the flora and fauna developing in these environments, as studied in other estuaries by Linderfelt and Turner (2001), Smith and Turner (2001) and Werner and Lockington (2006).

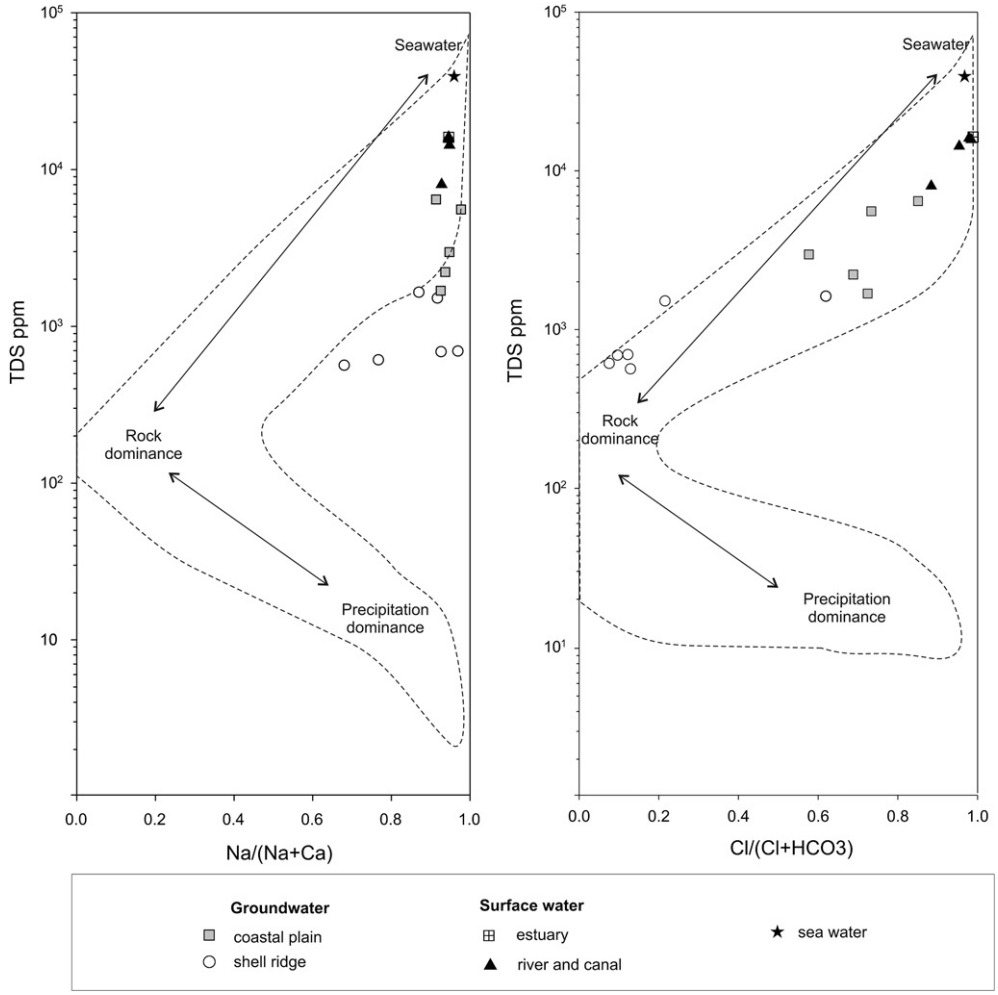

Fig. 7. Gibbs (1970) diagrams.

6. Conclusions

Shell ridges are characterized by the presence of groundwater of low salinity (below 1 g/L), constituting the only source of freshwater in the region. The morphology of the ridges and the high hydraulic conductivity of the sediments enable a fast infiltration of rainfall excess, which recharges groundwater. The chemical characteristics of this hydrological unit are determined by $CO_{2(g)}$, carbonate dissolution, and ion exchange.

In the coastal plain, groundwater is saline and its chemical characteristics are mainly determined by water inflow from the estuary and, to a lesser extent, by the dissolution (halite and gypsum) or oxidation (pyrite) of the mineral components of the sediment.

The composition of surface waters shows a strong tidal influence, which is wedge-shaped and has an average of 45% seawater in its composition.

From a hydrochemical perspective, the shell ridges, coastal plain, and surface watercourses and canals constitute particularly distinctive hydrological units. On these peculiarities depends the development of an ecosystem regarded as a natural reserve having unique characteristics that must be environmentally preserved. This is the reason why it has acquired special significance, not only because of the freshwater of shell ridges – which is the basis of water supply to the population – but also because of the saline surface water and groundwater of the coastal plain – which allows the development of most biological components of the wetland (*i.e., Spartina*, crabs, etc).

The knowledge contributed regarding the hydrogeochemical processes which determine the chemical composition of groundwater and surface water will be of use to identify management criteria and succeed in the introduction of sustainable measures concerning natural resources and, in particular, water resources. Besides, this research offers tools for the hydrochemical study of coastal areas, which can be applied in other regions worldwide.

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References

APHA (American Public Health Association), 1998. Standard Methods for the Examination of Water and Wastewater, twentieth ed. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC.

Appelo, C., Postma, D., 2005. Geochemistry, Groundwater and Pollution, second ed. Balkema Publishers.

Balay, M.A., 1961. El Río de la Plata entre la atmósfera y el mar. Publicaciones del Servicio de Hidrografía Naval, Buenos Aires. H-612.

Bianchi, T., 2006. Biogeochemistry of Estuaries. Oxford University Press, Oxford.

Borrego, J., Morales, J.A., Pendón, J.G., 1992. Formación de sulfuro de hierro en estuarios actuales: algunas consideraciones genéticas. Geogaceta 11, 125–127.
Brown, C.J., Schoonen, M.A., Candela, J.L., 2000. Geochemical modeling of iron, sulfur, oxygen and carbon in a coastal plain aquifer. Journal of Hydrology 237, 147–168.
Canevari, P., Blanco, D.E., Bucher, E., Castro, G.Y., 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., Pousa, J., 2008. Environmental hydrogeology of the southern sector of the Samborombón bay wetland, Argentina. Environmental Geology 54, 95–102.
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. Journal of Hydrology 365, 335–345.
César, I., Armendáriz, L., Becerra, R., 2005. Bioecology of the fiddler crab Uca uruguayensis and the burrowing crab *Chasmagnathus granulatus* (Decapoda, Brachyura) in the Refugio Vida Silvestre Bahía Samborombón, Argentina. Hydrobiologia 545, 237–248.
Deluchi, M., Forte Lay, J., Kruse, E., Laurencena, P., Carol, E., Rojo, A., 2006. Balance hidrológico en un sector de la costa oriental de la Provincia de Buenos Aires. In: VIII Congreso Latinoamericano de Hidrología Subterránea.
De Montety, V., Radakovitch, O., Vallet-Coulomb, C., Blavoux, B., Hermitte, D., Valles, V., 2008. Origin of groundwater salinity and hydrogeochemical processes in a confined coastal aquifer: case of the Rhone delta (Southern France). Applied Geochemistry 23, 2337–2349.
Fucks, E., Schnack, E., Aguirre, M., 2010. Nuevo ordenamiento estratigráfico de las secuencias marinas del sector continental de la Bahía Samborombón, provincia de Buenos Aires. Revista de la Asociación Geológica Argentina 67, 27–39.
Gibbs, R., 1970. Mechanisms controlling world water chemistry. Science 170, 1088–1090.
Guerrero, R., Acha, E., Framiñan, M., Lasta, C., 1997. Physical oceanography of the Río de la Plata Estuary, Argentina. Continental Shelf Research 17, 727–742.
Giménez, E., Morell, L., 1997. Hydrochemical analysis of salinization processes in the coastal aquifer of Oropesa (Castellón, Spain). Environmental Geology 29, 119–131.
Jorgensen, N., 2002. Origin of shallow saline groundwater on the Island of Laeso, Denmark. Chemical Geology 184, 359–370.
Linderfelt, W., Turner, J., 2001. Interaction between shallow groundwater, saline surface water and nutrient discharge in a seasonal estuary: the Swan-Canning system. Hydrological Processes 15, 2631–2653.
Logan, W., Nicholson, R., 1998. Origin of dissolved groundwater sulphate in a coastal plain sediments of the Río de la Plata, Argentina. Aquatic Geochemistry 3, 305–328.
Morse, J.W., Thomson, H., Finneran, D.W., 2007. Factors controlling sulfide geochemistry in sub-tropical estuarine and bay sediments. Aquatic Geochemistry 13, 143–156.
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. Journal of Hydrology 315, 93–116.
Otero, X.L., Macías, F., 2002. Caracterización y clasificación de suelos de las marismas de la Ría de Ortigueira en relación con su posición fisiográfica y vegetación (Galicia-NO de la Península Ibérica). Edafología 8, 37–61.
Parkhurst, D.L., Appelo, C.A.J., 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, p. 310.
Pires, L.C., Lacerda, L.D., 2008. Piritas framboidais associadas ao biofilme em sedimentos de Manguezal de Coroa Grande, Baía de Sepetiba, RJ. Geochimica Brasiliensis 22, 201–212.
Sala, J., González, N., Hernández, M., 1978. Efectos de una barrera hidráulica natural en las aguas subterráneas del litoral de la Bahía de Samborombón. In: Obra del Centenario del Museo de La Plata, vol. IV, pp. 153–166.
Silva-Filho, E.V., Sobral Barcellos, R.G., Emblanch, C., Blavoux, B., Sella, S.M., Daniel, M., Simler, R., Wasserman, J.C., 2009. Groundwater chemical characterization of a Rio de Janeiro coastal aquifer, SE – Brazil. Journal of South American Earth Sciences 27, 100–108.
Smith, A.J., Turner, J.V., 2001. Density-dependent surface water–groundwater interaction and nutrient discharge in the Swan-Canning Estuary. Hydrological Processes 15 (13), 2595–2616.
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.
Werner, A., Lockington, D., 2006. Tidal impacts on riparian salinities near estuaries. Journal of Hydrology 328, 511–522.