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Quaternary marine ingressions as indicated by hydrogeochemical evidence in the semi-confined aquifer of the littoral of the Río de la Plata, Argentina

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Abstract

The Quaternary is characterized by the occurrence of significant climate oscillations that led to noticeable sea-level changes. On the basis of hydrochemical indicators, the origin of the water salinity in the semi-confined aquifer in the region of the middle Río de la Plata estuary, Argentina is determined. Exploration wells were drilled and sediments were sampled for mineralogical analysis alongside water samples collected to determine major and minor ions and environmental isotopes in the aquifer. The Plio-Pleistocene fluvial sands in which the aquifer occurs are mainly composed of grains of quartz, feldspar, and mafic minerals. The water chemistry shows Na-Cl facies with a marked increase in salinity towards the Río de la Plata. The $\delta\ ^{18}O$ vs. $\delta\ ^{2}H$, Br^- vs. Cl^-, and $\delta\ ^{18}O$ vs. Cl^- ratios clearly trend towards seawater. Minor ions, such as Si, Sr, Li, Se, Br, and Rb, were the result of the prolonged interaction between the water that occurs in the aquifer and the mineral components of its matrix. The hydrogeochemical data show the marine origin of the saline water and that the hydrogeological evolution of the area during the Quaternary is as a result of sea-level oscillations.

Keywords: Hydrogeochemistry; Environmental isotopes; Pleistocene-Holocene Ingressions; Middle Río de la Plata estuary; Argentina

INTRODUCTION

In coastal areas, the interaction between groundwater and seawater is mainly evident in two processes: 1) groundwater discharge to the sea, and 2) marine ingression into coastal aquifers. In this area of interaction there is an interface, which is controlled by a series of factors such as the sea level, groundwater hydraulic heads, groundwater flow velocity, and differences in density, among others. In steady state systems or those in which equilibrium is reached rapidly between the sea level and aquifer hydraulic heads, the location of this interface can be easily predicted with analytical or numerical modeling (e.g., Werner et al., 2013). However, coastal environments are highly dynamic in nature, and are subjected to continuous geomorphic and hydrological evolution due to sea-level changes and variable sedimentation and erosion rates. The Quaternary is characterized by significant climate oscillations and marked sea-level changes (Phillips et al., 1986; Balbir et al., 1998; Rohling et al., 2008). Littoral deposits, coastal terraces, and paleocliffs provide evidence of sea-level change that occurred in the recent past in most coastal areas (Shackleton, 1987).

Changes in coastline position as a result of sea-level change cause an imbalance between the position of the groundwater and seawater interface and present-day sea level (Kooi and Groen, 2003; Morrissey et al., 2010; Lee et al., 2016). In many coastal areas worldwide, aquifers are not in equilibrium with the present-day sea level and, therefore, the position of the groundwater and seawater interface is a result of late Quaternary paleoenvironmental conditions (Groen et al., 2000; Kim et al., 2003; Bouchaou et al., 2009; El Yaouti et al., 2009; Somay and Gemici, 2009; Wang and Jiao, 2012; Post et al., 2013).

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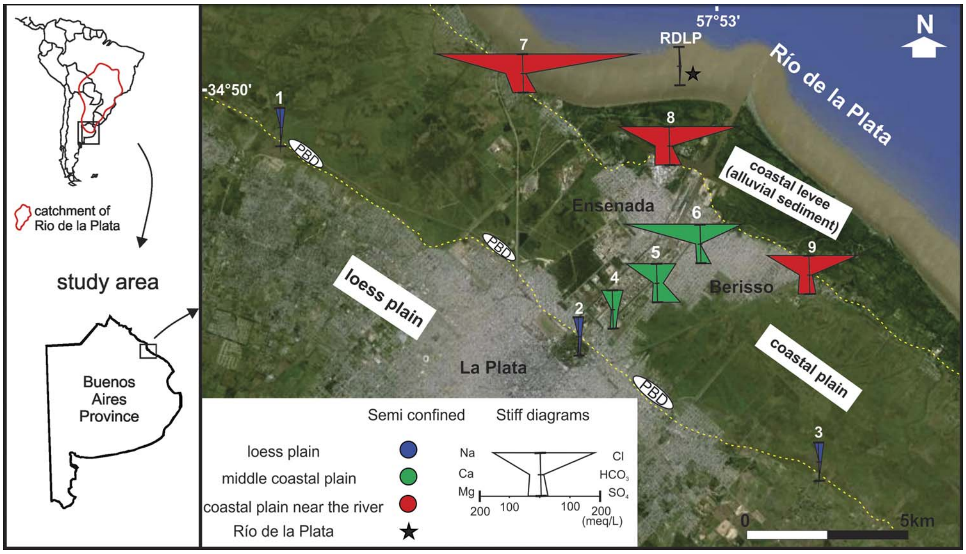

Figure 1. (color online). Location of the study area, geomorphic units, and sampling points (boreholes into the semi-confined aquifer and Río de la Plata). Stiff water type classification diagrams are indicated in each sampling point. Note that the Stiff diagram for Río de la Plata water is small and it cannot be clearly observed, however water in the Río de la Plata is of a sodium bicarbonate type. PBD, Pleistocene bioclastic deposits.

During sea-level rise, the coastline moves landward and the groundwater and seawater interface migrates in the shelf sector, allowing freshwater aquifers to occur in areas below the ocean (Lee et al., 2016). In search of equilibrium in the context of the new conditions, it is to be expected that seawater displaces this groundwater-and-seawater interface area landwards. Should the sea level fall, the aquifer fills with saltwater of marine origin. Over time the seawater is expected to migrate towards the ocean. The time it takes for equilibrium to be restored depends on the groundwater hydraulic head, velocity and flow volumes, geomorphology, types of sediments, and climate (Kooi et al., 2000).

Coastal marine deposits from the late Quaternary are present along the coastal regions of the Río de la Plata in Argentina (Schnack et al., 2005). In this area, a semi-confined aquifer occurs and is characterized by a marked increase in salinity in the coastal area near the Río de la Plata estuary. Since such Quaternary ingressions led to important changes in the geological, geomorphic, and hydrological evolution of the area, the objective of this work is to determine, on the basis of hydrochemical indicators, the origin of the water salinity in the semi-confined aquifer and its relationship with former environmental conditions.

STUDY AREA

The shoreline along the middle Río de la Plata estuary in Argentine is ~100 km long. The study area is located on

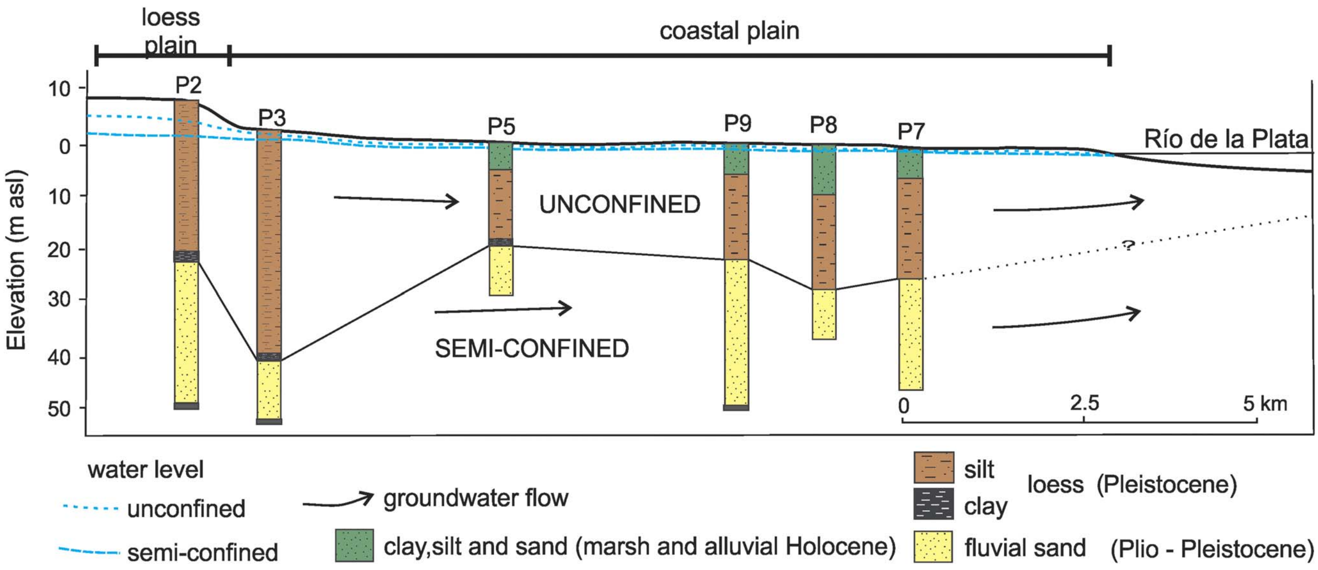

Figure 2. Hydrogeological profile.

the southwest margin of the middle Río de la Plata estuary and comprises a coastal strip ~10 km wide along the coastal cities of Ensenada and Berisso (Fig. 1). The Río de la Plata estuary has a microtidal regime with semidiurnal oscillations and a tidal wave range below 2 m. The water salinity varies between 1 and 2 g/L (Kind, 2004). The climate in the region is humid temperate with an annual mean precipitation of 1010 mm and a mean annual temperature of 16.2°C (1900–2012; Carol et al., 2012).

The semi-confined aquifer is situated in fluvial sediments mainly composed of fine- to medium-grained quartz sands (Kruse et al., 2013). Pleistocene loess sediments overlay the sands, which appear as an extensive loess plain in the continental sector (Fidalgo et al., 1975). The recharge of the semi-confined aquifer occurs through the local and indirect unconfined aquifer of the loess plain where the groundwater flow is towards the Río de la Plata. In the loess plain, the semi-confined aquifer provides the main source of water for the region and is of the low-salinity sodium bicarbonate type (below 1.5 g/L). Towards the coastal plain the water is salinized and becomes a sodium chloride type (Logan et al., 1999).

The sea-level highstand during the Late Pleistocene reached a height of ~6 m above mean sea level (AMSL) (Schnack et al., 2005). This highstand resulted in the formation of a coastal ridge composed of bioclastic sediment (Fig. 1). These ridges were partially eroded, at present being preserved as isolated forms (Fidalgo et al., 1973; Fucks et al., 2010). Holocene marine deposits are extensively distributed along the entire coast, at heights up to 5 m AMSL. These deposits are composed of fine-grained tidal plain and marsh environment sediments, and coastal ridges are composed of sand and shells.

METHOD

A monitoring network was designed to study the hydrodynamic and hydrochemical features of the semi-confined aquifer. This network was specially set up to monitor the hydrochemical parameters. Nine boreholes were drilled into the semi-confined aquifer to form the monitoring network, and included locations ranging from the coastal plain to the area adjacent to the loess plain (Fig. 1). A water circulation rotary drill was used to drill the boreholes, which were fitted with a 4-inch polyvinyl chloride casing. The boreholes were drilled up to a depth of approximately 60 m, reaching the base of the semi-confined aquifer. Along the entire thickness of the aquifer, a continuous filter and a well-sorted siliceous gravel prefilter was fitted, and the section of the unconfined aquifer was cemented. An automatic level (Kern GK1-AC) was used to set the zero level of every well with respect to the mean sea level. The lithology was described and the sediment samples were examined under a binocular magnifying glass as the boreholes were drilled. Sediment samples were taken every meter along the entire thickness of the semi-confined aquifer. Some samples were selected for mineralogical determination using X-ray diffraction (Philips X'Pert PRO).

Groundwater levels were determined in every well within the network with a manual probe. Water samples were obtained

Table 1. Physicochemical data. Abbreviations: SC, semiconfined aquifer; SW, seawater; RDLP, Río de La Plata.

		Well	pH	Cond (µS/cm)	STD (mg/L)	HCO_3 (mg/L)	SO_4 (mg/L)	Cl (mg/L)	Mg (mg/L)	Ca (mg/L)	K (mg/L)	Na (mg/L)	Se (µg/L)	Si (µg/L)	Sr (µg/L)	Li (µg/L)	Rb (µg/L)	Br (µg/L)	$\delta\,^{18}O$ (‰)	$\delta\,^{2}H$ (‰)
Loess plain	SC	P1	7.6	2180	1439	430	79	583	30	50	20	467	8.8	32424	666.72	31.3	5.94	1996	−5.81	−29.53
		P2	7.4	2600	1742	484	189	621	58	86	15	504	10.5	37183	1217.98	42.8	6.23	2009	−5.59	−28.29
		P3	7.5	2290	1443	484	11	586	37	73	16	428	6.7	30384	960.87	39.1	5.07	1935	−5.79	−29.11
Middle coastal plain	SC	P4	7.45	4820	3370	441	341	1200	110	137	30	921	-	88300	2061	80	16	7500	−5.34	−27.36
		P5	7.0	12030	10226	1271	3750	2100	221	350	62	3063	70	96900	3994	200	23	9900	−4.01	−21.11
		P6	12.7	14760	6790	311	1326	3200	12	79	986	2812	80	82400	5690	1550	3410	13300	−4.27	−24.39
Coastal plain near the river	SC	P7	7.0	30200	25972	312	2123	10700	1020	1436	109	6323	300	83400	15960	300	31	41000	−3.44	−18.61
		P8	6.9	23900	17925	505	2065	7700	700	1000	101	5298	170	86700	11114	240	28	27300	−3.67	−19.11
		P9	6.9	16950	11860	362	1080	5900	523	675	64	2891	130	87500	8342	210	23	22400	−4.60	−24.94
	SW		8.2	50000	35000	104	2669	19000	1350	410	390	10500	0.09	6400	8000	170	120	67000		
	RDLP		8.09	392	500	199.1	29.9	42	6.59	16.08	7.19	67.24	0.5	9100	138.65	6.9	6.39	142	−3.58	−21.77

from the wells and surface samples of the Río de la Plata in the coastal area for chemical analysis. Every well was washed before sampling: a volume of water three times larger than the well volume was extracted by means of a submersible pump. Water samples were preserved, and analysed for major ions (HCO_3^-, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, and K^+) following the standard methods of the American Public Health Association (APHA, 1998). Analytical errors were all <10%. Minor ions and trace elements (Si, Sr, Li, Se, Br, and Rb) were analysed using inductively coupled plasma mass spectrometry. Laser spectroscopy using Los Gatos Research equipment provided δ^{18}O and δ^{2}H results (Lis et al., 2008). These are reported in δ (‰) relative to V-SMOW (Gonfiantini, 1978) and the analytical uncertainties were ±0.3‰ and ±1‰ for ^{18}O and ^{2}H, respectively.

RESULTS

The semi-confined aquifer occurs in well-sorted, medium- to fine-grained Plio-Pleistocene fluvial sands and its thickness varies between 12 and 30 m. The medium-grained sands are mainly composed of rounded quartz grains (over 90%), with minor amounts of feldspar. Quartz also dominates, together with feldspar and mafic minerals (amphiboles), in the finest sand fraction. This aquifer is overlain by a phreatic aquifer situated in the Pleistocene silty and silty-clayey loess. The loess is separated from the semi-confined aquifer by a 3-m-thick clayey layer that acts as an aquitard. The loess deposit pinches out towards the Río de la Plata coast, where it is overlain by 31.5 m of Quaternary silty-clayey intertidal sediments. At the margin of the Río de la Plata, these intertidal deposits are overlain by present-day levee deposits composed of fine-grained sands (Fig. 2).

The piezometric levels in the semi-confined aquifer show that the flow is from the loess plain to the Río de la Plata. The phreatic aquifer level in the loess plain area is 0.2 m above the level of the semi-confined aquifer, which points to the occurrence of a downward vertical flow through the aquitard. This difference in levels decreases towards the Río de la Plata, which, together with the occurrence of finer sediments, does not causes any significant downward vertical flow (Fig. 2).

The major ion content in the semi-confined aquifer is predominantly sodium chloride facies with a marked increase in salinity (and in Na^+ and Cl^- content) from the loess plain towards the Río de la Plata (Fig. 1). Salt contents range between 1439 and 1742 mg/L in the loess plain, while in the middle coastal plain they measure between 3370 and 10226 mg/L, and in the coastal plain area adjacent to the Río de la Plata they measure between 11860 and 25972 mg/L (Table 1). Note that the Stiff diagram for Río de la Plata water is small and it can not be clearly observed (Fig. 1), however water in the Río de la Plata is of a sodium bicarbonate type with a salinity of 500 mg/L (Table 1).

δ^{18}O and δ^{2}H show isotopic enrichment from the loess plain to the coastal plain near the river. In the loess plain, δ^{18}O varies between −5.8 and −5.6‰, and δ^{2}H between −29.50 and −28.30‰, with the samples falling along the local meteoric water line (Fig. 3a). The coastal plain samples deviate from the meteoric line (Fig. 3a), and show isotopic enrichment towards seawater. In the middle sector of the coastal plain, δ^{18}O have values between −5.30 and −4.0‰, and δ^{2}H between −27.30 and −21.10‰. This corresponds to 8 to 30% seawater. In the sector near the river, δ^{18}O ranges between −4.60 and −3.4‰, and δ^{2}H between −24.90 and −18.60‰. These isotopic ratio enrichments correspond to 18 to 40% seawater (Fig. 3a). The Río de la Plata sample also shows isotopic enrichment with a trend towards seawater, with seawater close to 35%. However, as discussed below, due to other chemical characteristics, the isotopic enrichment observed in this sample is the result of evaporation processes and not of marine ingression.

Samples from the loess plain sector and the one of the Río de la Plata show low Cl^- and Br^- concentrations (Fig. 3b). The coastal plain sector samples have Br^- values between 7500 B and 13,300 µg/L, and in the sector adjacent to the river between 22,400 B and 41,000 µg/L. This increase is associated with a rise in Cl^- towards seawater (Fig. 3b). Such a Cl^- increase is also evident in the relationship between δ^{18}O and Cl^-, with the seawater percentages described above (Fig. 4a).

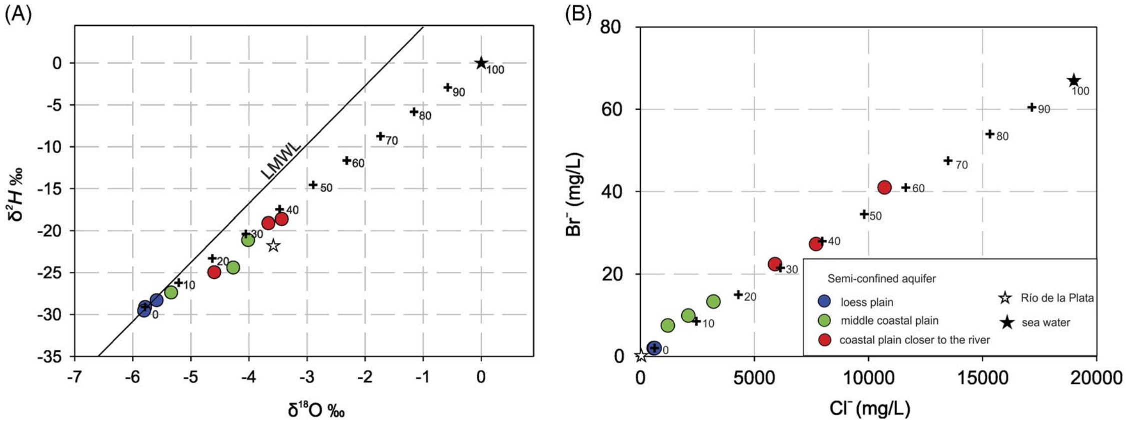

Figure 3. (A) $\delta\ ^{2}$H:$\delta\ ^{18}$O ratio, the local meteoric line (LMWL) corresponds to Panarello and Paricia (1984). (B) Br^-:Cl^- ratio. Black crosses represent percentages of mixture of semi-confined aquifer water from the loess plain to seawater (at intervals of 10%). (For interpretations of the references to color in this figure legend, the reader is referred to the web version of this article.)

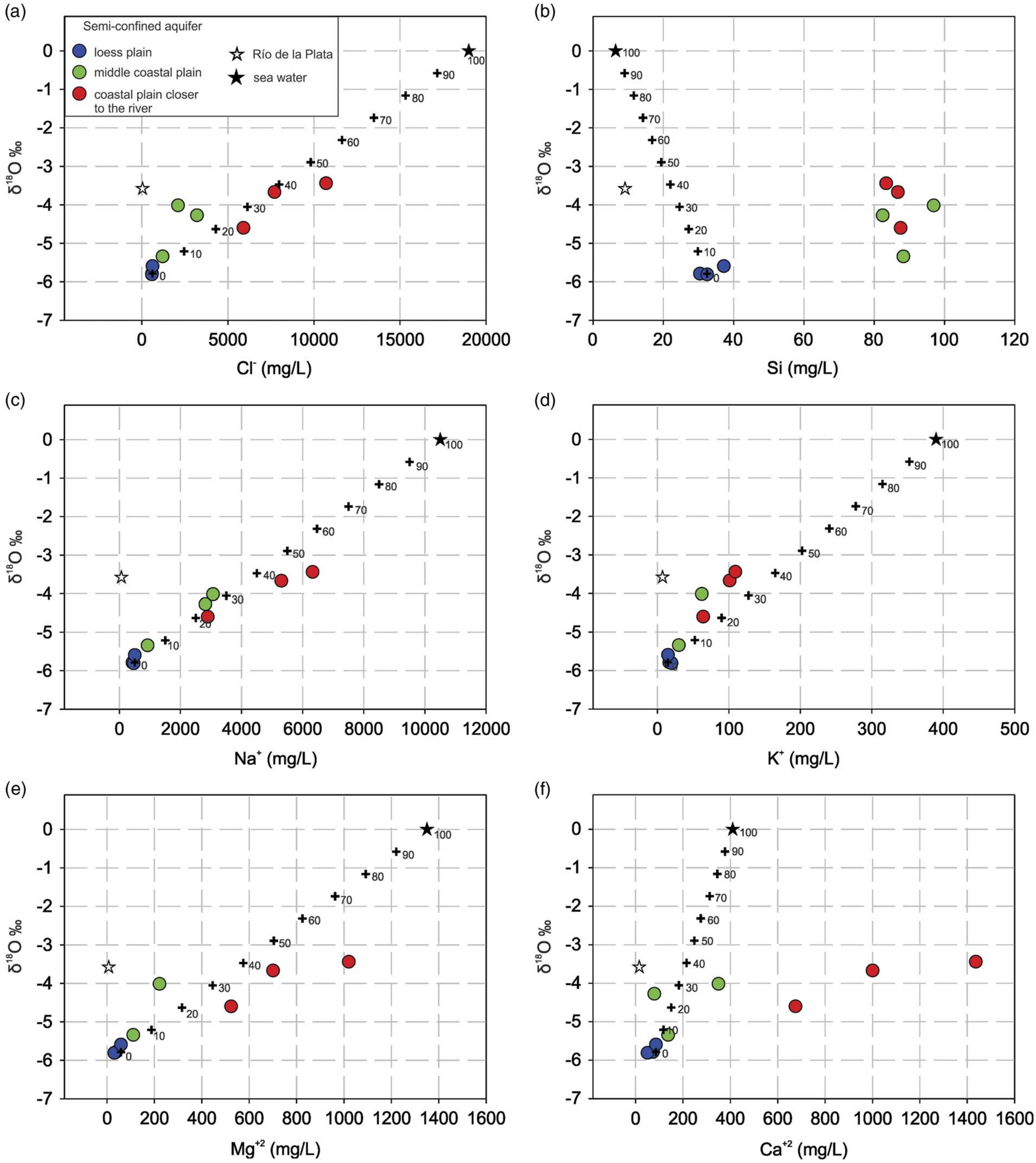

Figure 4. δ ^{18}O:ion ratios. Black crosses represent percentages of mixture of semi-confined aquifer water from the loess plain to seawater (at intervals of 10%). (For interpretations of the references to color in this figure legend, the reader is referred to the web version of this article.)

Considering that the main mineral components of the semi-confined aquifer are silicates, when the isotopic variation (δ ^{18}O) as a function of Si (Fig. 4b) is analyzed, it can be observed that the coastal plain samples deviate from the seawater mixing line. This is because these samples have a higher concentration of Si, with values between 80 and 100 mg/L, which duplicate those of the loess plain samples (between 20 and 40 mg/L). Na^+ is the most abundant major cation, showing with respect to the δ ^{18}O content a distribution according to the seawater mixing (Fig. 4c). Even though K^+ follows the same trend towards seawater, a displacement can be observed in the coastal plain samples towards values that indicate a deficiency of such a cation with respect to δ ^{18}O (Fig. 4d). In the plots for δ ^{18}O as a function of Mg^{+2} (Fig. 4e) and Ca^{+2} (Fig. 4f), the opposite situation is evident, mainly in the samples of the coastal plain adjacent to the river, which deviate from the trend towards seawater due to the fact that they have higher contents in such cations, mainly Ca^{+2}. It should be noted that the Río de la Plata sample deviates from the trends observed in the semi-confined aquifer water.

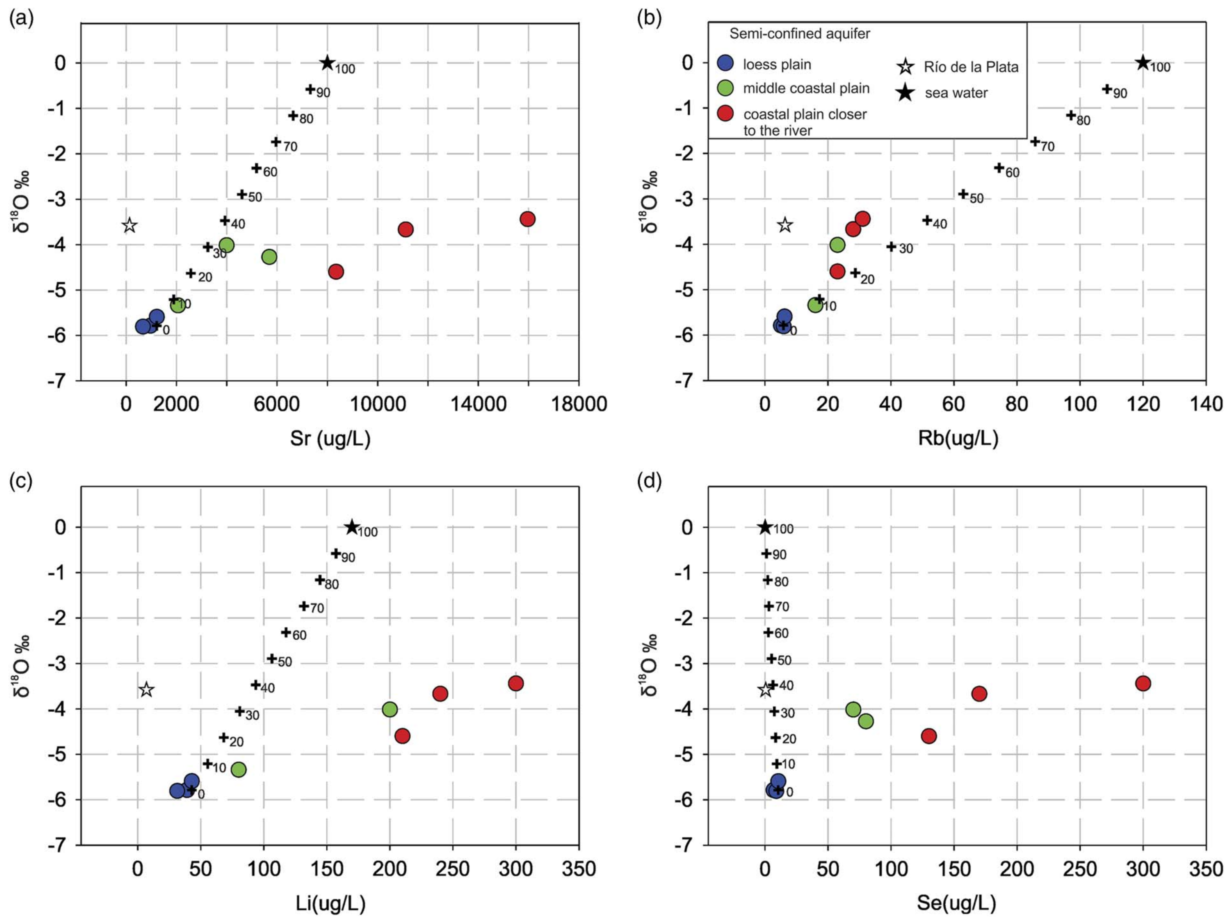

Figure 5. δ ^{18}O:ion ratios. Black crosses represent percentages of mixture of semi-confined aquifer water from the loess plain to seawater (at intervals of 10%). (For interpretations of the references to color in this figure legend, the reader is referred to the web version of this article.)

The δ ^{18}O contents as a function of the minor ions show, in the case of Sr and Rb, a trend similar to the one observed for Ca^{+2} and K^+, respectively (Fig. 5a and b). The coastal plain samples show an increase in Li and Se with respect to the values that the theoretical mixing with seawater should have, with the highest concentrations being observed in the samples closest to the Río de la Plata (Fig. 5c and d). As in the case of the major ions, the Río de la Plata sample deviates from the trends observed in the semi-confined aquifer water.

DISCUSSION

The semi-confined aquifer samples in the coastal plain area have δ ^{18}O vs. δ ^{2}H, Br^- :Cl^-, and δ ^{18}O:Cl^- ratios that clearly trend towards seawater. Such a trend does not correlate with the one of the Río de la Plata, which, even though it is isotopically similar in the δ ^{18}O:Cl^- ratios, deviates from the theoretical seawater mixtures. This suggests that the Río de la Plata water does not have an influence on the chemistry of the semi-confined aquifer. On the other hand, the semi-confined aquifer samples of the loess plain sector have isotopic content and Br^- values that follow the meteoric line, characteristics that show that this sector of the aquifer is recharged by rainfall. For all these reasons, and considering that the sea flooded the coastal plain area during late Quaternary ingressions, the semi-confined aquifer water may derive from the seawater of these ingressions. Only a percentage close to 10% remains of such seawater in the middle sector of the coastal plain and up to 40% in the sector near the river. This is due to the fact that it has been partially diluted by the fresh groundwater flow from the loess plain.

The preservation of a percentage of seawater originating from the Quaternary marine ingressions is evidence for a slow flow in the semi-confined aquifer and a strong water-mineral interaction in the sediment by the prolonged residence time. This interaction amplifies the dissolution processes, which are also promoted by the increase in the ionic strength of water as a result of the marine ingression (Appelo and Postma, 2005). The dissolution of the silicates such as quartz, plagioclase, feldspar, and amphibole within the aquifer is evident from the relationships between δ ^{18}O and Si, major cations, and minor ions. In these ratios, deviations with respect to the seawater mixing line can be observed, which suggests that there are ion gains and losses as a result of the rock-water interaction.

Silicate dissolution is significant in the entire marine ingression area (Fig. 4b), mainly for quartz, the main component of the aquifer. The contributions of Na and Mg to groundwater from the dissolution of plagioclase (in the case of Na) and amphibole (for both ions) are minor (Fig. 4c and e). Lithium, which is diadochic with Na in these minerals, also shows an increase in the marine ingression area (Fig. 5c). The largest increase is noted for Ca (Fig. 4f), probably caused by the incongruent hydrolysis of plagioclase and the dissolution of carbonates. It should be noted that Sr, which is in diadochy with Ca, exhibits a similar behaviour (Fig. 5a); however, its increase in concentration in the water is lower because it is a minor ion. Both Li and Sr are ions that, on entering into solution, behave as conservative ions in water, which is why they are good indicators of residence time of water in the aquifer. If water from a Quaternary marine ingression remains today in the aquifer, it is to be expected that its Li and Sr concentrations increase depending on the length of the time of contact of seawater with the aquifer matrix (Brondi et al., 1973; Tulipano and Fidelibus, 1984; Sola et al. 2014). In the case of K and Rb (diadochic in feldspar structures), even though they may be contributed to the water by the incongruent hydrolysis of K feldspar, their concentration decreases with respect to the theoretical mixture with seawater (Figs. 4d and 5b), indicating that both are retained in the solid matrix of the aquifer. On the other hand, Se tends to be desorbed from the solid phase of the aquifer at a pH close to 8 and, when entering into solution, it forms oxyanions that increase their concentration as the rock-water contact time increases (Massee and Maessen, 1981; Vengosh, 2003). Finally, given that the present-day water in the semi-confined aquifer represents a mixture of seawater and freshwater recharged by precipitation, it is not possible to undertake water dating that would assign an accurate age, as it is not a closed system. However, tritium data obtained in previous studies with values below 1 UT show that it is not present-day water (Dapeña, 2007).

The occurrence of past marine ingression is registered in confined and semi-confined aquifers in coastal areas in other regions of the world (Groen et al., 2000; Kim et al., 2003; Bouchaou et al., 2009; El Yaouti et al., 2009; Somay and Gemici, 2009; Wang and Jiao, 2012). Unlike other regions in which present-day seawater contributions may occur, geochemically the coastal areas of the Río de la Plata have no connection with the present-day freshwater occurring in the estuary.

CONCLUSIONS

Major and minor ions and environmental isotopes show that seawater that originated in Quaternary marine ingressions is still present in the groundwater of the semi-confined aquifer in the Río de la Plata estuary.

The $\delta^{18}O:\delta^{2}H$, $Br^{-}:Cl^{-}$, and $\delta^{18}O:Cl^{-}$ ratios show a clear trend towards seawater, which does not correlate with that of the Río de la Plata estuary, a present-day coastal water. In the coastal plain area, the semi-confined aquifer water contains between 8 and 40% seawater. The minor ion enrichment, which is the result of a prolonged interaction between the water in the aquifer and the mineral components of its matrix, makes it possible to establish that it is water with a long residence time. The semi-confined aquifer water may have originated in ingressions of seawater when the sea flooded the coastal plain area during the Late Quaternary.

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