



Identification of palaeo-seawater intrusion in groundwater using minor ions in a semi-confined aquifer of the Río de la Plata littoral (Argentina)



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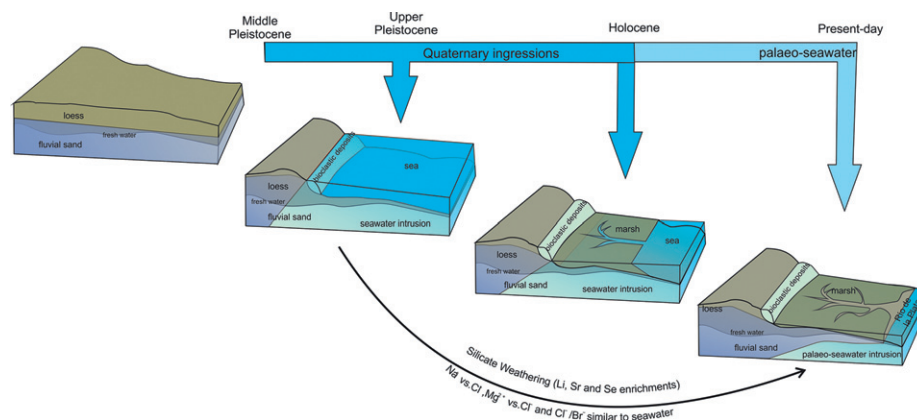
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HIGHLIGHTS

- The semi-confined aquifer in a sector of the Río de la Plata estuary is salinized.
- Saline content is higher in the aquifer than in the estuary.
- Minor elements indicate the occurrence of palaeo-seawater intrusion.
- Palaeo-seawater intrusion may be associated with interglacial fluctuations.

GRAPHICAL ABSTRACT



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ABSTRACT

The hydrochemistry of minor elements and traces such as bromide, lithium, strontium, uranium and selenium, together with the chemical analysis of major ions, has been used in the study of salinization process. This process occurs in a semi-confined aquifer that corresponds to a Pliocene–Pleistocene fluvial environment. The semi-confined aquifer is located in the littoral of the cities of Ensenada and Berisso, in the region of the middle Río de la Plata estuary, Argentina. Groundwater salinization was detected in the semi-confined aquifer in the coastal plain area, with salt contents that increase from the loess plain towards the river. The content of major ions that predominate in sea water (Cl^- , Na^+ and Mg^{2+}), as well as the Cl^-/Br^- and U vs. Cl^- ratios, demonstrates that such salinization is related to sea water, which shows no correspondence with estuary water. In the salinized area, Li, Sr and Se enrichments occur, and are used as tracers of the average time that a substance remains in solution in sea water in the aquifer. The study of such minor ions together with the geological evolution of the area made it possible to recognize that the salt water in the semi-confined aquifer corresponds to a palaeo-intrusion of sea water associated with the Pleistocene–Holocene ingressions caused by the climate changes occurring during the Quaternary.

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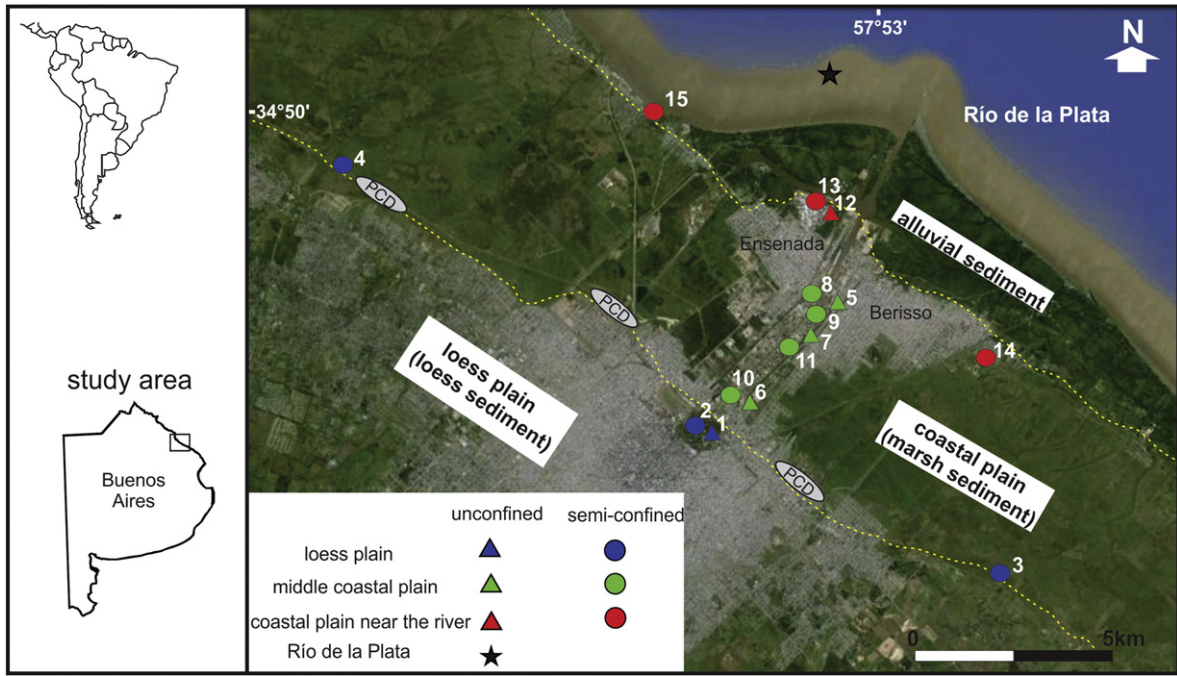


Fig. 1. Location of the study area and monitoring points. PBD: Pleistocene bioclastic deposits.

1. Introduction

Seawater intrusion into aquifer systems is a natural phenomenon occurring in many coastal plains (e.g., Todd and Mays, 2005). Climate changes (i.e. eustacy, temperature and precipitation changes) and ground vertical movements (i.e. subsidence and uplift), both natural

and man-induced, drive the advance and retreat of the fresh water/salt water interface (Kruse and Mas Pla, 2009). Among the causes of groundwater contamination, salinization is one of the processes that threaten the quality of coastal freshwater reserves and restrict their uses. Groundwater exploitation, especially in densely populated coastal areas, is often the cause of seawater intrusion towards the mainland

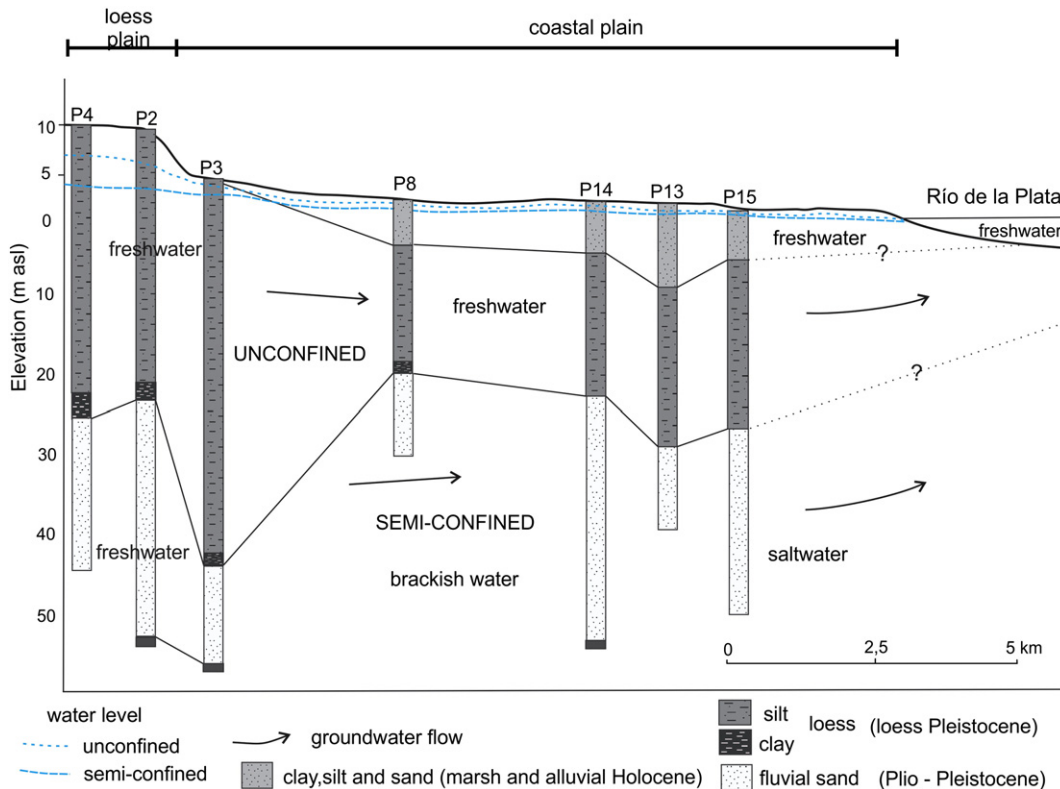


Fig. 2. Hydrogeological profile (cross-section from wells P4 to P15). The location of the wells is shown in Fig. 1.

(Lloyd et al., 1982; Kim et al., 2003; Capaccioni et al., 2005; Giambastiani et al., 2007; Trabelsi et al., 2007; Somay and Gemici, 2009).

Other processes, such as industrial contamination or wastewater (Ghabayen et al., 2006), the return flow of irrigation water (Milnes and Renard, 2004; Knapp and Baerenklau, 2006), the dissolution of evaporitic materials or the contribution of marine aerosol, especially in semi-arid regions (Andreasen and Fleck, 1997; Cruz and Silva, 2000; Cartwright et al., 2004), may also induce the salinization of groundwater. As a consequence of future sea-level rise, an increase in aquifer salinization is expected in many coastal plains (Sherif and Singh, 1999; Kundzewicz et al., 2007; Döll, 2009; Carretero et al., 2013).

Hydrogeochemical studies aiming at explaining the anthropogenic or natural processes that determine aquifer salinization are of great importance to develop sustainable management guidelines for water resources. The relationships between major ions and ¹⁸O and ²H isotopes are widely used tools in the evaluation of salinization processes (Kim et al., 2003; Capaccioni et al., 2005; Carol et al., 2009; Gattaceca et al., 2009; El Yaouti et al., 2009; Mollema et al., 2013; Re et al., 2013; Alvarez et al., 2015; Da Lio et al., 2015). There are cases in which the relationship between major ions and isotopes is not a determinant, as in the case of the overlapping of different processes or the presence of palaeo-seawater. In such cases, the use of minor elements and traces has proven to be an efficient tool to understand the salinization mechanisms of aquifers directly related to sea water (Giménez and Morell, 1991; Gimenez and Morell, 1997; Sanches-Martos et al., 2002; Faye et al., 2004; Somay and Gemici, 2009).

The cities of Ensenada and Berisso are located in the inner coastland in the middle Río de la Plata estuary (Argentina) (Fig. 1). This area is

densely populated and fresh water for different purposes is supplied by the Río de la Plata and a semi-confined aquifer. In the middle estuary of this river, low salinity water occurs, with values below 2 g/L (Guerrero et al., 1997). The semi-confined aquifer is characterized by its low saline content (less than 1.5 g/L) and high productivity in the continental area, with its salinity greatly increasing, up to 10 g/L, towards the vicinity of the river (Sala and Hernandez, 1969; Sala et al., 1982).

The objectives of this work are to identify the origin of the salinization in the semi-confined aquifer on the basis of a hydrogeochemical evaluation mainly based on the analysis of minor ions and traces, and to assess its possible association with the geological evolution of the region. Coastal aquifer salinization is a problem that affects many cities worldwide; that is why it is so relevant to carry out tests in order to understand the processes that originate it. Therefore, the results obtained will be of relevance not only for the study area, but also for other regions in the world with similar hydrogeological characteristics.

2. Study area

The study area comprises a coastal strip approximately 10 km wide, located in the littoral of the cities of Ensenada and Berisso, on the right margin of the middle Río de la Plata estuary (Fig. 1). The estuary has a semidiurnal, microtidal regime, with water salinity varying in this section between 1 and 2 g/L (Guerrero et al., 1997). The area is characterized by a humid temperate climate, with a historical precipitation record (1900–2012) with an annual mean of 1010 mm and a mean annual temperature of 16.2 °C (Carol et al., 2012).

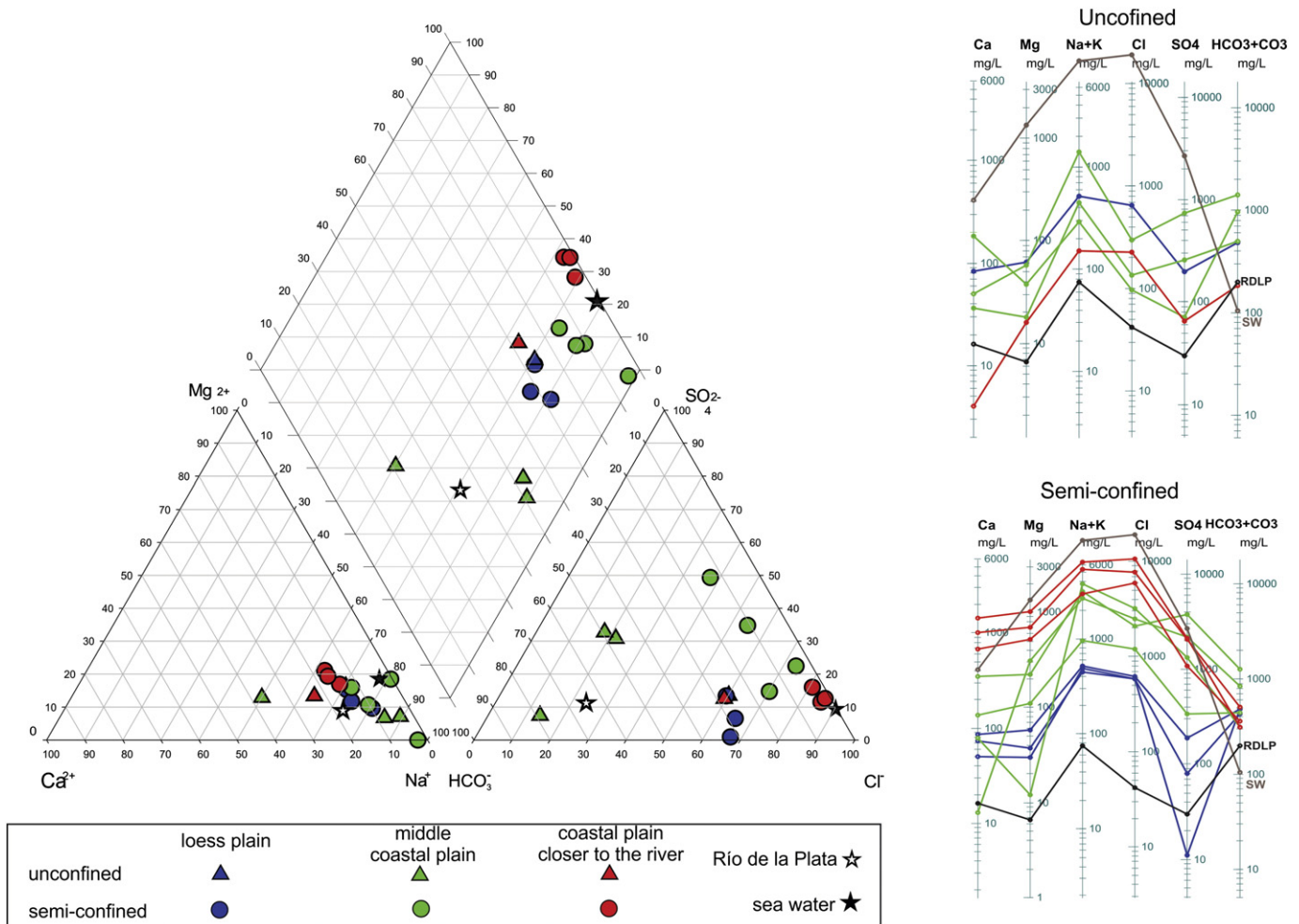


Fig. 3. Piper and Schoeller diagrams.

Table 1

Physicochemical data. UC: unconfined aquifer, SC: semi-confined 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)	U (µg/L)	Br (µg/L)	
Loess plain	UC	P1	7.4	2610	1749	484	196	645	62	84	15	498	10.5	39,061	1285.2	43.3	25.67	2060
	SC	P2	7.4	2600	1742	484	189	621	58	86	15	504	10.5	37,183	1217.98	42.8	25.59	2009
		P3	7.5	2290	1443	484	11	586	37	73	16	428	6.7	30,384	960.87	39.1	16.77	1935
Middle Coastal plain		P4	7.6	2180	1439	430	79	583	30	50	20	467	8.8	32,424	666.72	31.3	13.69	1996
	UC	P5	7.2	1935	1258	957	71	97	38	183	22	270	3.5	31,381	1314.62	14.9	12.75	1220
		P6	7.9	1842	1197	500	257	135	18	36	14	430	3.6	37,080	457.44	35.5	17.02	436
		P7	7.9	3800	2964	1406	737	300	58	50	33	1365	–	98,600	870	70.0	19.0	4700
	SC	P8	8.3	11,280	9024	844	2165	2500	310	13	206	2453	70	72,100	118	190	3.0	10,700
		P9	12.7	14,760	6790	311	1326	3200	12	79	986	2812	80	82,400	5690	155	–	13,300
		P10	7.45	4820	3370	441	341	1200	110	137	30	921	–	88,300	2061	80	7.0	7500
Coastal plain closer to the river		P11	7.0	12,030	10,226	1271	3750	2100	221	350	62	3063	70	96,900	3994	200	32	9900
	UC	P12	7.0	1105	597	183	65	227	16	4	11	140	1.4	13,859	385.13	7.8	0.17	614
		P13	6.9	23,900	17,925	505	2065	7700	700	1000	101	5298	170	86,700	11,114	240	10.0	27,300
	SC	P14	6.9	16,950	11,860	362	1080	5900	523	675	64	2891	130	87,500	8342	210	6.0	22,400
		P15	7.0	30,200	25,972	312	2123	10,700	1020	1436	109	6323	300	83,400	15,960	300	7.0	41,000
SW			8.2		35,000	104	2669	19,000	1350	410	390	10,500	0.09	6400	8000	170	3.0	67,000
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	0.59	142

The semi-confined aquifer occurs in Plio-Pleistocene fluvial sediments mainly composed of fine- to medium-grained quartz sands (Kruse et al., 2013). These are overlain by loess sediments deposited during the Pleistocene, outcropping in the continental sector in an extensive loess plain (Fidalgo et al., 1975). In the more littoral sectors, sea-level oscillations during the Quaternary led to the deposition of marine sediments that reworked the abrasion

platform in the loess plain (Schnack et al., 2005). The early marine deposits are from the Middle to Late Pleistocene and correspond to coastal barriers deposited in a high-energy environment and cropping out in the limit with the loess plain (Fig. 1). In turn, the Holocene deposits, which overlie most of the area, correspond to clayey silts of tidal plain environments, overlain by present-day alluvial deposits in the vicinity of the river (Fig. 1).

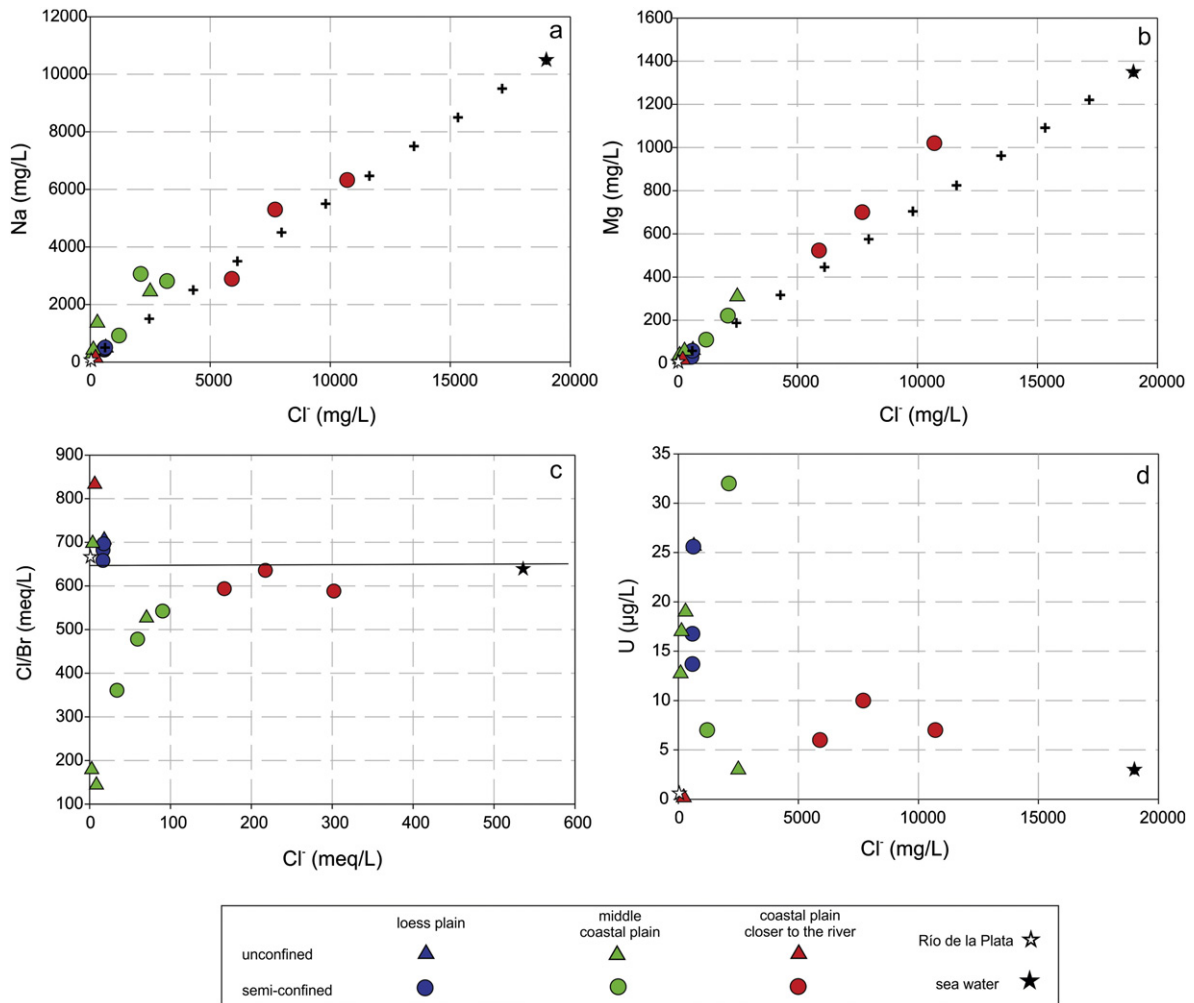


Fig. 4. Ion ratios. Black crosses represent percentages of mixture of semi-confined aquifer water from the loess plain and sea water (at intervals of 10%).

An unconfined aquifer occurs both within the loess plain sediments and those of the coastal plain, and it is separated from the semi-confined aquifer by a clayey layer (aquitar). Precipitation is the source of recharge to the unconfined aquifer, whose regional groundwater flow is towards the Río de la Plata (Carol et al., 2013). On the loess plain, groundwater in the unconfined aquifer is a low-salinity sodium bicarbonate type. In the coastal plain, groundwater in the unconfined aquifer has highly variable compositions: it may be a sodium chloride to sodium bicarbonate type, with a high-salinity sulphate type in sectors (Logan et al., 1999; Ainchil et al., 2004). In the semi-confined aquifer in the loess plain, low-salinity sodium bicarbonate type water occurs (below 1.5 g/L) and it constitutes the main source of water supply in the region. The salt content is modified towards the coastal plain, where water is

salinized and it becomes a sodium chloride type (Logan et al., 1999; Ainchil et al., 2004). The recharge of the semi-confined aquifer is local and indirect from the unconfined aquifer on the loess plain and the groundwater flow is towards the Río de la Plata.

3. Methodology

Due to the fact that in some sectors of the study area the groundwater is characterized by high salinity, there are no available supply wells or boreholes for hydrochemical monitoring; therefore, it was necessary to set up a monitoring network specifically for this study. The network consists in fifteen monitoring sites in which boreholes were drilled at

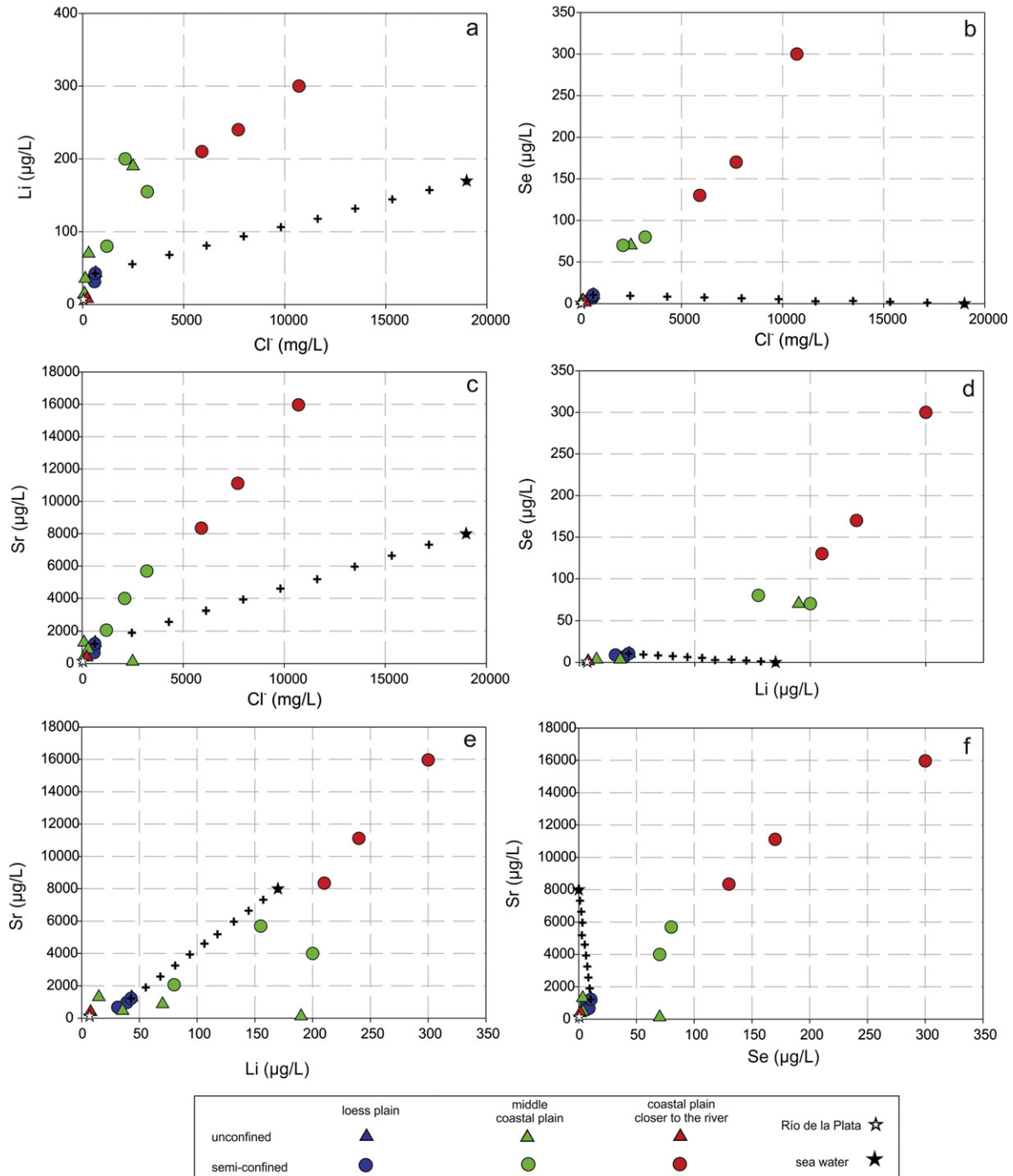
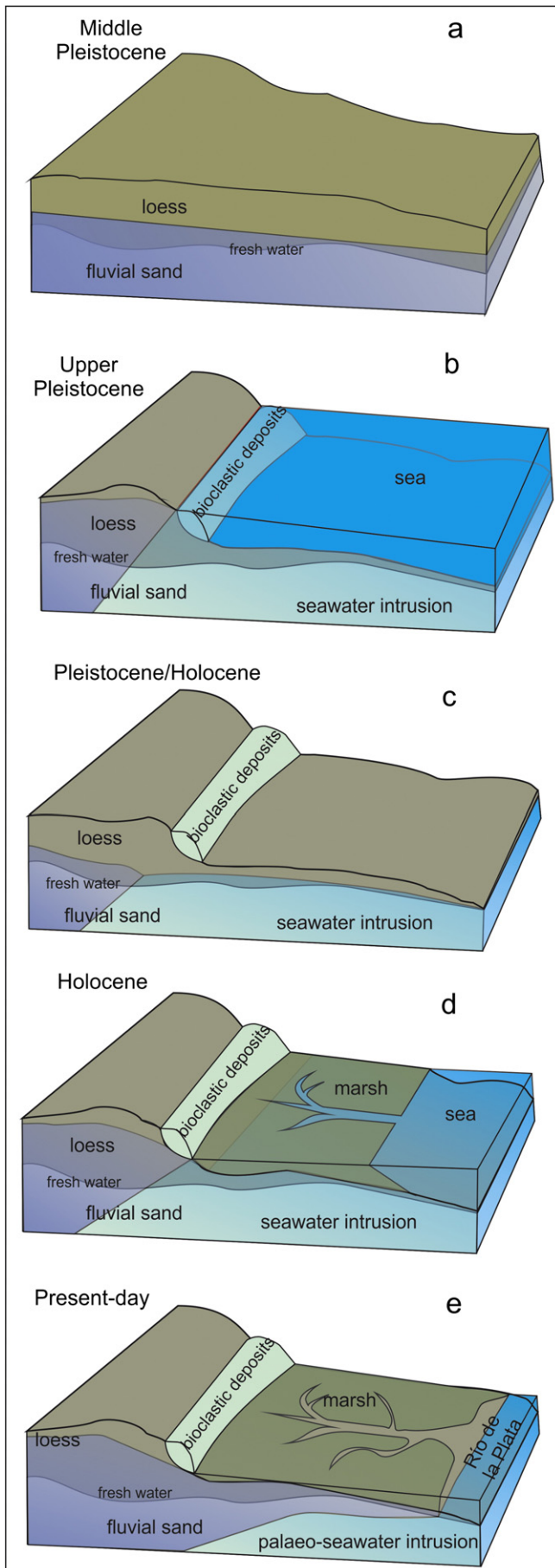


Fig. 5. Ion ratios. Black crosses represent percentages of mixture of semi-confined aquifer water from the loess plain and sea water (at intervals of 10%).



the level of both aquifers, covering the coastal plain and the zone adjacent to the loess plain (Fig. 1).

The boreholes were drilled with a water circulation rotary drill and fitted with a 4-in. PVC casing. In the case of the semi-confined aquifer, the drilling reached the base of the aquifer (approximately 60 m deep), and a continuous filter and a well-sorted siliceous gravel prefilter were fitted along the entire aquifer thickness, cementing the section of the unconfined aquifer. The boreholes in the unconfined aquifer were drilled to a depth of 8 m, fitting a continuous filter and a siliceous gravel prefilter as well. The zero level of all wells was set with respect to the mean sea level with an automatic level (Kern GK1-AC).

During borehole drilling, the lithological description was made and sediment samples were obtained in order to undertake the mineralogical description under a magnifying glass of the sandy-silty fraction, as well as the hydrogeological characterization of the stratigraphic column. In every well of the monitoring network, the groundwater levels were measured with a manual probe and water samples were extracted for the chemical analysis; samples were also obtained from the Río de la Plata. Prior to the sampling of every well, they were washed by means of the extraction of a water volume over three times larger than the well volume, using a submersible pump. The collection, preservation and major ion chemical analyses (HCO_3^- , Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ , K^+) of the water samples were carried out according to the standard methods outlined by the American Public Health Association (APHA, 1998). Minor ions and traces (Sr, Li, U, Se, Br) were analyzed by means of the inductively coupled plasma mass spectrometry (ICP-MS) technique. These ions were chosen because they allow the verification of the processes originating a seawater intrusion (Fakir et al., 2002; Faye et al., 2004). The use of such natural tracers has acquired relevance in recent years as a tool to understand the mechanisms causing the mineralization and salinization of aquifers (Andreasen and Fleck, 1997; Somay and Gemici, 2009). The data presented in this work correspond to the monitoring carried out in June 2015; however, quarterly monitoring of major ions and levels was performed, observing no considerable variations between the samplings.

4. Results

4.1. Hydrogeological and hydrodynamic characteristics

Based on the data obtained from the wells, the thickness and lithological characteristics of each aquifer unit could be identified. In the loess plain area, the unconfined aquifer occurs in silty and silty-clayey sediments with carbonate concretions whose average thickness is 32 m. The minerals predominating in the silt fraction are quartz, feldspars, amphiboles and volcanic glass. Towards the coastal plain, these sediments wedge out and are overlain by sediments of intertidal origin, with a silty-clayey grain size, as well as seashell and fine sand intercalations in sectors. In the sand fraction, the main minerals are quartz, feldspars, carbonates and amphiboles. The average thickness of these sedimentary deposits is up to 10 m.

Underlying the loess deposits, there is a silty-clayey layer of limited thickness (3 m), which hinders the hydraulic transmission between the unconfined aquifer and the semi-confined aquifer. Below this layer, the semi-confined aquifer occurs, mainly composed of well-sorted, fine- to medium-grained sand with a thickness ranging from 12 to 30 m. The medium to coarse sand grains are composed of quartz and, to a lesser extent, feldspars, whereas in the finer fraction opaques and amphiboles can be recognized.

The groundwater level measurements undertaken in the unconfined and semi-confined wells indicate that in both cases the groundwater flow is from the loess plain towards the Río de la Plata. When the levels of both aquifers are compared at the same point, it can be observed that

Fig. 6. Diagram of hydrogeological evolution during the Quaternary and formation of the palaeo-seawater intrusion.

the unconfined aquifer is higher with respect to the semi-confined aquifer; that is to say, a descending vertical flow occurs. In the area adjacent to the loess plain, the water table is 1.5 m above the level of the semi-confined aquifer. Towards the vicinity of the river, such a difference decreases to values of a few centimetres, indicating a decrease with respect to the descending vertical flow (Fig. 2). This trend between levels would indicate that the semi-confined aquifer discharges slowly into the Río de la Plata, ruling out the possibility that the river is at present contributing water to the aquifer.

4.2. Hydrochemistry

The chemical composition of groundwater shows variations from the loess plain adjacent to the coastal plain towards the sector of the coastal plain closer to the river. In the first case, both unconfined water and semi-confined aquifer water are a sodium chloride type with salt contents between 1439 and 1749 mg/L (Fig. 3, Table 1). In the middle sector of the coastal plain, unconfined water differs from semi-confined aquifer water not only in its salinity, but also in its hydrochemical facies. In the unconfined aquifer, water is a sodium bicarbonate to calcium bicarbonate type with salinities between 1197 and 2964 mg/L, whereas in the semi-confined aquifer it is a sodium chloride type with a salt content between 3370 and 10,226 mg/L. In the sector of the coastal plain closer to the river, the samples are of a sodium chloride type with a salinity of 597 mg/L in the unconfined aquifer and from 11,860 to 25,972 mg/L in the semi-confined aquifer. On the other hand, water in the Río de la Plata is of a sodium bicarbonate type with a salinity of 500 mg/L (Table 1). Note that in the Schoeller diagram it can be clearly observed that the characteristics of semi-confined aquifer water trend towards sea water—both unrelated to that of the Río de la Plata—from the loess plain sector to the coastal plain (Fig. 3).

There is an increasing trend in the salt content associated with the increase in chloride concentration (Table 1). Río de la Plata water is the one showing the lowest chloride concentration (42 mg/L), whereas in groundwater the lowest values occur in unconfined water (between 97 and 645 mg/L). A noticeable increase in Cl^- content takes place in semi-confined aquifer water from the loess plain (583 mg/L) to the sectors close to the river (10,700 mg/L), which is accompanied with an increase in Na^+ with a trend towards sea water (Fig. 4a). Considering these ions as being characteristic of sea water, and putting together a theoretical mixture of semi-confined aquifer water from the loess plain and sea water, the groundwater of the semi-confined aquifer from the middle coastal plain shows between 5 and 20% sea water in its composition. On the other hand, in the samples obtained closer to the river, water from the semi-confined aquifer has between 27 and 56% sea water in its composition. In the ratio between Cl^- and Mg^{2+} —the second most important cation in sea water—a tendency towards sea water is also observed, with similar percentages to the ones described above, but with a slight deviation towards higher Mg^{2+} contents (Fig. 4b). Similarly, the samples show an increase in Cl^- , with Cl^-/Br^- ratio values similar to the ones of sea water (Fig. 4c). A decrease in U content is also noticeable, with values resembling those of sea water (Fig. 4d). It should be noted that, regarding both the Cl^-/Br^- ratio and U content, the values in the Río de la Plata do not show any correspondence with those of the semi-confined aquifer or with the ones of sea water.

As regards the minor and trace elements Li, Se and Sr, it can be observed that, even though their concentration tends to rise as Cl^- increases, in all cases there is a deviation with respect to the seawater mixing line (Fig. 5a–c). This deviation is caused by an enrichment in such minor ions from the middle coastal plain to the sector closer to the river, as it happens with Cl^- . Se concentrations are higher than those of sea water in the samples from the semi-confined aquifer, both on the middle coastal plain and in the vicinity of the river (Fig. 5d and f). In turn, Li and Sr concentrations increase linearly from that

of sea water only in the semi-confined aquifer water corresponding to the sector of the coastal plain closer to the river (Fig. 5e). On the other hand, the Río de la Plata sample shows the lowest concentrations of all these minor ions.

5. Discussion

The concentrations of the major ions that dominate in sea water (Cl^- , Na^+ and Mg^{2+}), as well as the Cl^-/Br^- ratio suggest that the salinization occurring in the semi-confined aquifer water of the coastal plain is related to sea water. The seawater percentages increase from 5% on the middle coastal plain to 56% in the areas close to the river. In the littoral of the cities of Ensenada and Berisso, the marine origin of the salinization was indicated in previous works undertaken in the region, according to isotope and major ion determinations (Sala and Hernandez, 1969; Dapeña, 2007; Ainchil, 2009). The salinization of the semi-confined aquifer in the loess plain due to its intensive exploitation is justified by the advance of the salt water contained in such an aquifer in the coastal plain area. Unlike other coastal areas, in this case it should be taken into consideration that the middle Río de la Plata estuary has an average salinity below 1.5 g/L (Guerrero et al., 1997), which is why the advance of salt water cannot originate in the estuary. This can be verified in the comparison of the compositions of Río de la Plata water and those of semi-confined aquifer water, which show highly dissimilar hydrochemical characteristics.

Certain minor ion contents, such as those of Li, Sr and Se, make it possible to verify the processes originating seawater intrusion (Fakir et al., 2002; Faye et al., 2004). Li and Sr are ions that, when entering into solution, remain in water as conservative ions, which is why this is a good indicator of residence time of water in the aquifer. These elements may be supplied by the dissolution of the amphiboles and feldspars that compose the matrix of the semi-confined aquifer. If water originating from seawater intrusion has high temporal permanence in the aquifer, it is to be expected that its Li and Sr concentrations should rise as the contact time between sea water and the aquifer matrix increases (Brondi et al., 1973; Tulipano and Fidelibus, 1984; Gosselin et al., 2004; Somay and Gemici, 2009). On the other hand, Se is an abundant element in coastal plain sediments and it tends to be desorbed from the solid phase of the aquifer to pH values close to 8. When it enters into solution, it forms oxyanions that increase Se concentration as the water–rock contact time increases (Massee and Maessen, 1981; Vengosh, 2003).

Such characteristics show that the Li, Sr and Se ions may be used as tracers for residence time. It should be noted that, in semi-confined aquifer water from the middle coastal plain sector and the one closer to the river, Li, Sr and Se enrichments were registered. These minor ion contents as a function of Cl^- show an enrichment with respect to the theoretical seawater mixture, with higher contents in the samples from the littoral area than those of sea water (Fig. 5a–c). In turn, this characteristic can be verified more clearly in the ratios between the minor ions (Fig. 5d–f).

In view of the above, it is expected that if sea water (in the salt wedge area) were in contact with the aquifer matrix for long periods, there would be an enrichment of these minor ions (Gimenez and Morell, 1997). In this way, the enrichment observed in the minor ions with respect to the seawater mixture would show that the semi-confined aquifer water from the coastal plain corresponds to a palaeo-seawater intrusion.

On the other hand, the ratio between U and Cl^- contents also indicates the marine origin of the semi-confined aquifer water, but in this case there is a decrease in U in the seawater intrusion area. The coastal aquifers in the area of the seawater interface tend to decrease in U content, mainly in the sectors in which the marsh areas develop (Duncan and Shaw, 2003). Salt marshes are geochemically very active environments, with U retention in the sites in which continental groundwater and sea water interact (Church et al., 1996). Therefore, it is to be

expected for the semi-confined aquifer water to be associated with a seawater intrusion in which marsh environments developed.

The presence of palaeo-seawater intrusions has been recorded in confined and semi-confined aquifers in coastal areas in other regions worldwide (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 the examples in the above-mentioned works, the case of the study area differs in that the saltwater aquifer is in contact with a surficial freshwater body and not sea water. It is to be expected for such palaeo-seawater intrusion to be associated with global climate changes that occurred during the Quaternary.

Based on evidence related to the geological evolution (Figini et al., 1977; Fidalgo, 1979; Fidalgo et al., 1981; Nabel and Vargas, 1993; Codignotto and Aguirre, 1993; Cavalotto, 2002; Aguirre and Whatley, 1995; Schnack et al., 2005), it is possible to explain the origin of the palaeo-seawater intrusion into the semi-confined aquifer. The fluvial sandy sediments occurring in this aquifer deposited during the Plio-Pleistocene. These are overlain by loess sediments deposited during the Lower–Middle Pleistocene, constituting the loess plain (Fig. 1 and Fig. 6a). In the Upper Pleistocene, approximately 120,000 years ago, the marine incursion related to the last interglacial maximum occurred. The sea covered the study area up to the present-day height of 7 m.a.s.l., leaving high-energy bioclastic deposits over the current border area between the continental and the coastal plain (Fig. 1 and Fig. 6b). This marine incursion reworked the abrasion platform in the loess sediments and sea water entered the Plio-Pleistocene sandy fluvial sediments that at present constitute the semi-confined aquifer. This seawater incursion formed a salt wedge that covered the area of the present-day coastal plain. It was followed by a cold arid period, which caused the retreat of the sea level and a new loess sediment deposition (Fig. 6c). In such an arid environment, the seawater wash-out due to rainwater infiltration or groundwater flow towards the sea was a process of limited relevance. The Holocene incursion—related to isotope stage 1—developed coastal plain deposits, which were reworked and deposited over the loess sediments. Low-energy sediments composed of clayey silt dominated the coastal plain, associated with marsh environments. With a smaller extension, high-energy deposits composed of shells and sand were deposited in coastal barrier environments. This incursion caused another seawater intrusion in the sandy fluvial sediments that, in turn, was limited above by the low-permeability deposits of the tidal plain environments (Fig. 6d).

Currently, in the area close to the Río de la Plata, a sandy levee with present-day river deposits has developed. This sector is under tidal influence, with the unconfined aquifer that occurs in the levee area showing low-salinity water, whereas in the middle sector of the coastal plain water tends to have a higher salt content. In the semi-confined aquifer, the palaeo-seawater intrusion is mainly preserved in the areas close to the river. A wash-out of this palaeo-seawater intrusion occurs towards the continental area, mainly due to the fresh groundwater flow that enters laterally from the loess plain. To a lesser extent, the vertical infiltration of water from the unconfined aquifer may also contribute to the wash-out of the salt wedge (Fig. 6e).

6. Conclusion

The minor ion (Li, Sr, Se, U and Br) ratios and contents made it possible to identify that the salinization recorded in the semi-confined aquifer in the coastal plain area is the result of palaeo-seawater intrusion. Similarly, the more conservative major ions (Cl^- , Na^+ and Mg^{2+}) were useful to generate theoretical mixtures and to determine the percentage of sea water present in the palaeo-seawater intrusion. These data related to the geological evolution of the area during the Quaternary allowed the development of a conceptual model of geohydrological evolution of the seawater intrusion and its preservation at present, even though it is adjacent to the middle Río de la Plata estuary, where water has a low salinity.

The results obtained show that the traces of the marine regressions and transgressions occurring during the Pleistocene–Holocene are not only evident in the sedimentary sequences, but they have also left their signature in groundwater. The characteristics observed are not inherent to the area, but they explain processes that may occur at a global level as a result of the sea-level oscillation during the Quaternary.

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References

- Aguirre, M.L., Whatley, R.C., 1995. Late Quaternary marginal marine deposits and palaeoenvironments from northeastern Buenos Aires Province, Argentina: a review. *Quat. Sci. Rev.* 14, 223–254.
- Ainchil, J., 2009. Coastal Plain in northeastern Buenos Aires Province: hydrogeological characteristics [dissertation] Ca' Foscari University, Venezia, Italy.
- Ainchil, J., Calahorra Fuertes, P., Kruse, E., 2004. Variaciones químicas del flujo subterráneo en la planicie costera próxima a La Plata, Argentina. *Proceedings: Groundwater Flow Understanding. XXXIII (Congress IAH – 7^o Congress Alhsud. T2–31. Zacatecas (México))*.
- Alvarez, M., Carol, E., Dapeña, C., 2015. The role of evapotranspiration in the groundwater hydrochemistry of an arid coastal wetland (Península Valdés, Argentina). *Sci. Total Environ.* 506–507, 299–307. <http://dx.doi.org/10.1016/j.scitotenv.2014.11.028>.
- Andreasen, D.C., Fleck, W.B., 1997. Use of bromide:chloride ratio to differentiate potential sources of chloride in a shallow, unconfined aquifer affected by brackish water intrusion. *Hydrogeol. J.* 5, 17–26.
- APHA (American Public Health Association), 1998. *Standard methods for the examination of water and wastewater*. 20th ed. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC.
- Bouchaou, L., Michelot, J.L., Qurtobi, M., Zine, N., Gaye, C.B., Aggarwal, P.K., Vengosh, A., 2009. Origin and residence time of groundwater in the Tadla basin (Morocco) using multiple isotopic and geochemical tools. *J. Hydrol.* 379, 323–338.
- Brondi, M., Dall'Aglio, M., Vitriani, F., 1973. Lithium as a pathfinder element in the large scale hydrogeochemical exploration for hydrothermal systems. *Geothermics* 2, 142–153.
- Capaccioni, B., Didero, M., Paletta, C., Didero, L., 2005. Saline intrusion and refreshing in a multilayer coastal aquifer in the Catania Plain (Sicily, Southern Italy): dynamics of degradation processes according to the hydrochemical characteristics of groundwaters. *J. Hydrol.* 307, 1–16.
- Carol, E., Kruse, E., Laurencena, P., Rojo, A., Deluchi, M., 2012. Ionic exchange in groundwater hydrochemical evolution. Study case: the drainage basin of El Pescado creek (Buenos Aires province, Argentina). *Environ. Earth Sci.* 65, 421–428.
- Carol, E., Kruse, E., Mancuso, M., Melo, M., 2013. Local and regional water flow quantification in groundwater-dependent wetlands. *Water Resour. Manag.* 34, 26–32. <http://dx.doi.org/10.1007/s11269-012-0216-9>.
- Carol, E., Kruse, E., Mas Pla, J., 2009. Hydrochemical and isotopic evidence of ground water salinization processes on the coastal plain of Samborombón Bay, Argentina. *J. Hydrol.* 365, 335–345. <http://dx.doi.org/10.1016/j.jhydrol.2008.11.041>.
- Carretero, S., Rapaglia, J., Bokuniewicz, H., Kruse, E., 2013. Impact of sea-level rise on salt-water intrusion length into the coastal aquifer, Partido de La Costa, Argentina. *Cont. Shelf Res.* 62, 62–70.
- Cartwright, I., Weaver, T.R., Fulton, S., Nichol, C., Reid, M., Cheng, X., 2004. Hydrogeochemical and isotopic constraints on the origins of dryland salinity, Murray Basin, Victoria, Australia. *Appl. Geochem.* 19, 1233–1254.
- Cavalotto, J.L., 2002. Evolución holocena de la llanura costera del margen sur del Río de la Plata. *Revista Asociación Geológica Argentina* 57, 376–388.
- Church, T.M., Sarin, M.M., Fleisher, M.Q., Ferdelman, T.G., 1996. Salt marshes: an important coastal sink for dissolved uranium. *Geochim. Cosmochim. Acta* 60, 3879–3887.
- Codignotto, J.O., Aguirre, y.M.L., 1993. Coastal evolution, changes in sea level and molluscan fauna in northeastern Argentina during the late Quaternary. *Mar. Geol.* 110, 163–176.
- Cruz, J.V., Silva, M.O., 2000. Groundwater salinization in Pico Island (Azores, Portugal): origin and mechanisms. *Environ. Geol.* 39, 1181–1189.
- Gosselin, D.C., Harvey, F.E., Frost, C., Stotler, R., Macfarlane, P.A., 2004. Strontium isotope geochemistry of groundwater in the central part of Dakota (Great Plains) aquifer, USA. *Appl. Geochem.* 19, 359–377.
- Da Lio, C., Carol, E., Kruse, E., Teatini, P., Tosi, L., 2015. Saltwater contamination in the managed low-lying farmland of the Venice coast, Italy: an assessment of vulnerability. *Sci. Total Environ.* 533, 356–369.
- Dapeña, C., 2007. *Isótopos ambientales livianos*. Universidad de Buenos Aires, Su aplicación en hidrología e hidrogeología.
- Döll, P., 2009. Vulnerability to the impact of climate change on renewable ground-water resources: a global-scale assessment. *Environ. Res. Lett.* 4. <http://dx.doi.org/10.1088/1748-9326/4/3/035006>.

- Duncan, T., Shaw, T.J., 2003. The mobility of rare earth elements and redox sensitive elements in the groundwater/seawater mixing zone of a shallow coastal aquifer. *Aquat. Geochem.* 9, 233–255.
- El Yaouti, F., El Mandour, A., Khattach, D., Benavente, J., Kaufmann, O., 2009. Salinization processes in the unconfined aquifer of Bou-Areg (NE Morocco): a geostatistical, geochemical, and tomographic study. *Appl. Geochem.* 24, 16–31.
- Fakir, Y., El Mernissi, M., Kreuser, T., Berjami, B., 2002. Natural tracer approach to characterize groundwater in the coastal Sahel of Oualidia (Morocco). *Environ. Geol.* 43, 197–202.
- Faye, S., Maloszewski, P., Stichler, W., Trimborn, P., Faye, S.C., Gaye, C.B., 2004. Groundwater salinization in the Saloum (Senegal) delta aquifer: minor elements and isotopic indicators. *Sci. Total Environ.*
- Fidalgo, F., 1979. Upper Pleistocene-recent marine deposits in Northeastern Buenos Aires Province (Argentina). *Proc. of the "1978 International Symposium on Coastal Evolution in the Quaternary"*, pp. 384–404.
- Fidalgo, F., De Francesco, F.O., y Pascual, R., 1975. *Geología superficial de la llanura bonaerense (Argentina)*. VI Congr. Geol. Arg. Relatorio, pp. 103–138.
- Fidalgo, F., Figini, A., Gómez, G., Carbonari, J., Huarte, R., 1981. Dataciones radiocarbónicas en las formaciones Las Escobas y destacamento Río Salado, provincia de Buenos Aires. *Actas VIII Congreso Geológico Argentino*. 4, pp. 43–56.
- Figini, A., Huarte, R., Gómez, G., 1977. Datación por radiocarbono con contador proporcional. *Obra del Centenario del Museo de la Plata, Geología*. IV, pp. 289–297.
- Gattacceca, J.C., Vallet-Coulomb, C., Mayer, A., Claude, C., Radakovitch, O., Conchetto, E., Hamelin, B., 2009. Isotopic and geochemical characterization of salinization in the shallow aquifers of a reclaimed subsiding zone: the southern Venice Lagoon coastland. *J. Hydrol.* 378, 46–61.
- Ghabayen, S., McKee, M., Kemblowski, M., 2006. Ionic and isotopic ratios for identification of salinity sources and missing data in the Gaza aquifer. *J. Hydrol.* 318, 360–373.
- Giambastiani, B.M., Antonellini, M., Essink, G.H.O., Stuurman, R.J., 2007. Saltwater intrusion in the unconfined coastal aquifer of Ravenna (Italy): a numerical model. *J. Hydrol.* 340, 91–104.
- Giménez, E., Morell, I., 1991. Consideraciones sobre la utilización de iones minoritarios en la caracterización de la intrusión marina. III SIAGA, pp. 401–412.
- Gimenez, E., Morell, I., 1997. Hydrogeochemical analysis of salinization processes in the coastal aquifer of Oropesa (Castellon, Spain). *Environ. Geol.* 29, 118–131.
- Groen, J., Velstra, J., Meesters, A., 2000. Salinization processes in paleowaters in coastal sediments of Suriname: evidence from d37Cl analysis and diffusion modelling. *J. Hydrol.* 234, 1–20.
- Guerrero, R., Acha, E., Framiñan, M., Lasta, C., 1997. Physical oceanography of the Rio de la Plata Estuary, Argentina. *Cont. Shelf Res.* 17, 727–742.
- Kim, Y., Lee, K., Koh, D., Lee, D., Lee, S., Park, W., Koh, G., Woo, N., 2003. Hydrogeochemical and isotopic evidence of groundwater salinization in a coastal aquifer: a case study in Jeju volcanic island, Korea. *J. Hydrol.* 270, 282–294.
- Knapp, K., Baerenklau, K.A., 2006. Ground water quantity and quality management: agricultural production and aquifer salinization over long time scales. *J. Agric. Resour. Econ.* 616–641.
- Kruse, E., Mas Pla, J., 2009. Hydrological processes and water quality in coastal aquifers. *Gestión Ambiental de Áreas costeras*. Rubes Editorial (España) 2, 29–54.
- Kruse, E., Carol, E., Mancuso, M., Laurencena, P., Deluchi, M., Rojo, A., 2013. Recharge assessment in an urban area: a case study of La Plata, Argentina. *Hydrogeol. J.* 21, 1091–1100.
- Kundzewicz, Z.W., Mata, L.J., Arnell, N.W., Döll, P., Kabat, P., Jiménez, B., Miller, K.A., Oki, T., Sen, Z., Shiklomanov, I.A., 2007. Fresh water resources and their management. In: Parry, M.L., Canziani, O.F., Palutikof, J.P., vander Linden, P., Hanson, C.E. (Eds.), *Climate Change 2007: Impacts, Adaptation and Vulnerability*. Contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK, pp. 173–210.
- Lloyd, J.W., Howard, K.W.F., Pacey, N.R., Tellam, J.H., 1982. The value of iodine as parameter in the chemical characterization of groundwaters. *J. Hydrol.* 57, 247–265.
- Logan, W., Auge, M., Panarello, H., 1999. Bicarbonate, sulfate and chloride water in a shallow, clastic-dominated coastal flow system, Argentina. *Ground Water* 37, 287–295.
- Massee, R., Maessen, F.J.M.J., 1981. Losses of silver, arsenic, cadmium, selenium and zinc traces from distilled water and artificial sea-water by sorption on various container surfaces. *Anal. Chim. Acta* 127, 181–193.
- Milnes, E., Renard, P., 2004. The problem of salt recycling and seawater intrusion in coastal irrigated plains: an example from the Kiti aquifer (Southern Cyprus). *J. Hydrol.* 288, 327–343.
- Mollema, P.N., Antonellini, M., Dinelli, E., Gabbianelli, G., Greggio, N., Stuyfzand, P.J., 2013. Hydrochemical and physical processes influencing salinization and freshening in Mediterranean low-lying coastal environments. *Appl. Geochem.* 34, 207–221.
- Nabel, P.E., Vargas, D., 1993. Magnetoestratigrafía de la Fm Pascua, Pleistoceno de la Pcia. de Bs.As. *Revista Asociación Geológica Argentina* 53, 557–561.
- Re, V., Sacchi, E., Martín-Bordes, J.L., Aureli, A., El Hamouti, N., Bouchnan, R., Zuppi, G.M., 2013. Processes affecting groundwater quality in arid zones: the case of the Bou-Areg coastal aquifer (North Morocco). *Appl. Geochem.* 34, 181–198.
- Sala, J.M., Hernandez, M.A., 1969. Estimación de algunos parámetros en base a la invasión de aguas saladas en la ciudad de La Plata. *Proc. Cuatras jornadas geológicas argentinas*, 7/15 Buenos Aires.
- Sala, J.M., Hernández, M.A., Kruse, E., 1982. Groundwater regime forecasting with inadequate data in Argentina. *IAHS – AISH Publication* 136, 314–324.
- Sanchez-Martos, F., Pulido-Bosch, A., Molina-Sanchez, L., Vallejos-Izquierdo, A., 2002. Identification of the origin of salinization in groundwater using minor ions Lower Andarax, (Southeast Spain). *Sci. Total Environ.* 297, 43–58.
- Schnack, E., Isla, F., De Francesco, F., Fucks, E., 2005. Estratigrafía del Cuaternario Marino Tardío en la Provincia de Buenos Aires. In: De Barrio, R., Etcheverry, R., Caballé, M., E., y L. (Eds.), *Geología y Recursos Minerales de la provincia de Buenos Aires*, 16° Congreso Geológico Argentino, Relatorio 159–182, La Plata.
- Sherif, M.M., Singh, V.P., 1999. Effect of climate change on seawater intrusion in coastal aquifers. *Hydrol. Process.* 13, 1277–1287.
- Somay, M.A., Gemic, Ü., 2009. Assessment of the salinization process at the coastal area with hydrogeochemical tools and geographical information systems (GIS): Selçuk plain, Izmir, Turkey. *Water Air Soil Pollut.* 201, 55–74.
- Todd, D.K., Mays, L.W., 2005. *Groundwater Hydrology*. third ed. John Wiley & Sons, Inc.
- Trabelsi, R., Zairi, M., Dhia, H.B., 2007. Groundwater salinization of the Sfax superficial aquifer, Tunisia. *Hydrogeol. J.* 15, 1341–1355.
- Tulipano, L., Fidelibus, M.D., 1984. Geochemical characteristics of Apulian coastal springs (southern Italy) related to mixing processes of ground waters with seawater having different residence time in to the aquifer. In: Tsakiris, G. (Ed.), *Proceedings, 5th International Conference on Water Resources Planning and Management*. Water in the year 2000. Athens.
- Vengosh, A., 2003. Salinization and saline environments. *Treatise on Geochemistry*. 9, pp. 333–365.
- Wang, Y., Jiao, J.J., 2012. Origin of groundwater salinity and hydrogeochemical processes in the confined Quaternary aquifer of the Pearl River Delta, China. *J. Hydrol.* 438, 112–124.