



Identifying and quantifying geochemical and mixing processes in the Matanza-Riachuelo Aquifer System, Argentina



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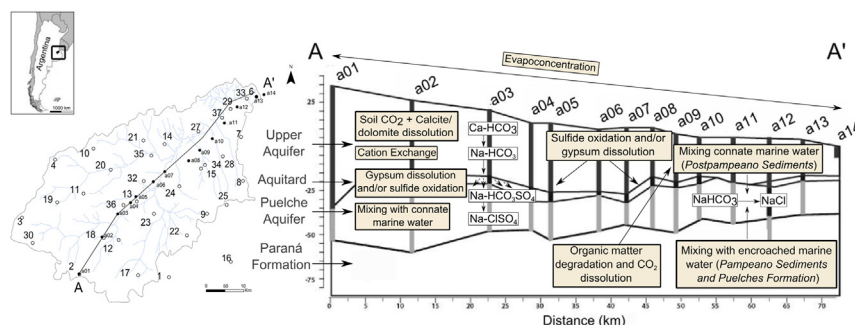
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HIGHLIGHTS

- The Matanza-Riachuelo River Basin is affected by severe water pollution problems.
- Groundwater chemistry origin has been studied using a multi-tool approach.
- A short suite of physico-chemical processes explain the groundwater composition.
- Marine groundwater with different age and location contribute to aquifer salinity.
- The existence of several sources of SO₄ has been deduced.

GRAPHICAL ABSTRACT



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ABSTRACT

The Matanza-Riachuelo River Basin, in the Northeast of the Buenos Aires Province, is one of the most industrialized and populated region in Argentina and it is worldwide known for its alarming environmental degradation. In order to prevent further damages, the aquifer system, which consists of two overlaid aquifers, is being monitored from 2008 by the river basin authority, Autoridad de la Cuenca Matanza-Riachuelo. The groundwater chemical baseline has been established in a previous paper (Zabala et al., 2016), and this one is devoted to the identification of the main physical and hydrogeochemical processes that control groundwater chemistry and its areal distribution. Thirty five representative groundwater samples from the Upper Aquifer and thirty four from the deep Puelche Aquifer have been studied with a multi-tool approach to understand the origin of their chemical and isotopic values. The resulting conceptual model has been validated through hydrogeochemical modeling. Most of the aquifer system has fresh groundwater, but some areas have brackish and salt groundwater. Water recharging the Upper Aquifer is of the Ca-HCO₃ type as a result of soil CO₂ and carbonate dissolution. Evapotranspiration plays a great role concentrating recharge water. After recharge, groundwater becomes Na-HCO₃, mostly due to cation exchange with Na release and Ca uptake, which induces calcite dissolution. Saline groundwaters exist in the lower and upper sectors of the basin as a result of Na-HCO₃ water mixing with marine water of different origins. In the upper reaches, besides mixing with connate sea water other sources of SO₄ exist, most probably gypsum and/or sulfides. This work highlights the relevance of performing detailed studies to understand the processes controlling groundwater chemistry at regional scale. Moreover, it is a step forward in the knowledge of the aquifer system, and provides a sound scientific basis to design effective management programs and recovery plans.

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1. Introduction

Groundwater resources, in terms of quality and quantity, is one of the most challenging current and future issues of concern in developing countries. The ever-increasing rate of population growth and the inherent water supply demand has led to intensive groundwater exploitation. Human concentration in large urban centers significantly modifies the water budget, particularly in those ones situated above productive aquifers. This is the case, for instance, of the metropolitan area of Buenos Aires city. Gathering 13,047,000 habitants (INDEC, 2010), it is the second largest metropolitan area in Latin America after Sao Paulo (21,242,939 habitants, IBGE, 2016).

Preservation of groundwater resources generally contrasts with a precarious or absent role of groundwater within the framework of a country's development strategy, which usually manifests by a poor legislation about water preservation and management. In Argentina, this lack of protection in past times led the Matanza-Riachuelo River Basin (MRB) (Fig. 1) to become one of the most industrialized and populated regions of the country, and one of the most polluted basins around the World (Mendoza et al., 2015).

Although the MRB supports 10% of Argentinian population, most of its surface water courses show severe contamination and even anoxia state as consequence of domestic and industrial wastewater discharges (ACUMAR, 2016).

Slaughterhouses, food and metal industries, tanning, oil and petrochemical factories, and meat-curing plants later replaced by industrial freezers, polluted the MRB surface and groundwater bodies for almost two hundred years (Ronco et al., 2008; Mendoza et al., 2015). On the other hand, after the 1970s, overexploitation of the Upper Aquifer induced an important depression of the piezometric levels, promoting the displacement of the saline water/fresh interface towards the continent and the contamination risk through pollutants migration derived from the inversion of the hydraulic gradients (Hernández, 1978; Santa Cruz, 1972; Bocanegra, 2005).

The environmental degradation in the MRB reached alarming levels, whereby in 2008 the Supreme Court of Justice of Argentina sentenced to the Matanza Riachuelo Basin Authority (Autoridad de Cuenca Matanza Riachuelo, ACUMAR) to take actions to improve the quality of life and the environment, and to prevent future damages in the basin (CSJN, 2008). In response, in 2008 ACUMAR designed and implemented the Integrated Environmental Sanitation Plan (Plan Integral de Saneamiento

Ambiental, PISA) and invested on surface water and groundwater monitoring networks. ACUMAR's groundwater network included the drilling and monitoring of 86, 91 and up to 102 boreholes in 2014, 2015 and 2017 respectively, devoted to characterize and understand the present-day and past groundwater quality conditions.

The first groundwater research activities of the PISA were focused on compiling the existent and available groundwater data, and on identifying the chemical baseline of the aquifer system (Zabala et al., 2016). Those authors studied the statistical difference of groundwater composition in 570 samples from the Upper Aquifer and 322 samples from the Puelche Aquifer taken between May 2008 and September 2011. They stated that groundwater chemical composition of both aquifers is quite stable in time in most of the system. In most of the aquifer system groundwater is of the Na-HCO₃ type, except in specific parts of the basin where it is of the Ca-HCO₃, Na-ClSO₄ and Na-Cl types. The work proposed potential hydrogeochemical processes responsible for the groundwater chemistry observed, but they were not checked. At present, ACUMAR's priority goals – to perform an efficient groundwater management and to apply the recovery plan – require a more detailed knowledge of the aquifer system hydrochemistry, including not only the leading hydrogeochemical processes, but also the less common processes and the location where they are occurring.

The main objective of this work is: (1) to propose a validated conceptual model capable of explaining the regional groundwater chemical composition of the Matanza-Riachuelo Aquifer System (MRAS); (2) to identify the areas where both the most and the less common hydrogeochemical processes are occurring, and (3) to support the numerical modeling work under way to develop a management toolset for the assessment of the MRAS groundwater resources (i.e., flow and transport numerical models). To achieve these objectives, a range a multi-tool approach has been used to identify the main physical and hydrogeochemical processes responsible for the different groundwater chemical signatures present in the MRAS, their spatial distribution, and their relative contribution to the regional hydrochemistry.

2. Study area

2.1. General features

The study area is the whole MRB. With a surface of 2,065 km², it extends between the Salado River basin to the SW and the Río de La Plata

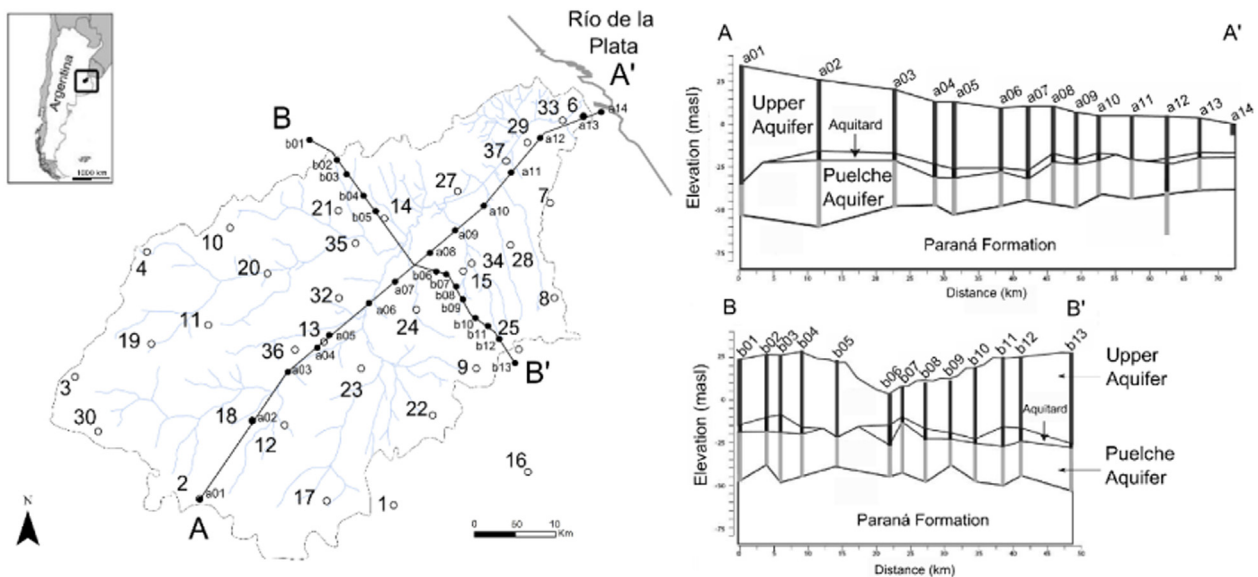


Fig. 1. Location of the study area and boreholes used for this work and for the two hydrogeological sections (A-A' and B-B') of the Matanza-Riachuelo Aquifer System. (Modified from Mancino et al., 2013.)

to the NE (Fig. 1). The main water course is the Matanza River, which flows NE along 70 km before to be renamed Riachuelo some 15 km to its discharge into the Río de La Plata.

The MRB, as the entire Buenos Aires Province, is characterized by a temperate climate with warm and hot summers and cold winters with regular winds from the E and NE. Average monthly precipitation shows a clear seasonality, with lower values in the cold season (May to September) and higher in the warm season (October to April). Also, there is a spatial rainfall variation from SW to NW that shows a positive correlation with distance to the coast. Thus, the highest annual precipitation is recorded at the lower basin. The National Meteorological Survey of Argentina reported 1193 mm/y at the Buenos Aires city and 1008 mm/y at the Ezeiza station, located at the middle basin, for the period 1956–2008.

Results from a watershed water balance in the Buenos Aires station using the Penman-Monteith method report a total of 1277 mm/y of potential evapotranspiration; – 137.6 mm of water deficit in summer and 53.5 mm of water excess in winter. This means that water deficit is the dominant situation in the soils of the MRB (Vives et al., 2012).

2.2. Geology and hydrogeology

The MRB sedimentary basin is mostly composed by fine continental and marine sediments deposited over a crystalline Precambrian basement. Four major sedimentary units with different hydrogeological features can be identified from bottom to top: (1) Olivos, (2) Paraná, and (3) Puelches formations, and (4) the set of Pampeano and Postpampeano sediments. The Olivos Formation is an Eocene to Early Miocene continental unit, sandy to the bottom and clayey to the top, with presence of gypsum (Auge, 1986, 2004). From the hydrogeological point of view, the clayey layers behave as an aquiclude, whereas the sandy layers behave as a moderate productivity aquifer (Auge et al., 2002). The Paraná Formation (marine origin, Miocene age) is mostly siliceous, with some gypsum and calcium carbonate (González Bonorino, 1965; Santa Cruz, 1972), and it holds connate marine water (Auge et al., 2002). Two sections with different hydraulic behavior can be identified: (1) a lower sandy section, which behaves as a confined aquifer, and an upper clayey section that behaves as an aquitard. Neither the Olivos Formation nor the Paraná Formation is intensively exploited in the MRB, mostly because they hold very saline water compared to the overlying formations. Only the Paraná Formation is locally exploited for industrial purposes. However, at local scale the Paraná Formation may influence the chemistry of the overlying Puelches Formation. The top of the Paraná Formation is just at 40 m depth in the NE of the MRB and at some 90 m depth in the SW (Mancino et al., 2013); its thickness varies between 13 and 323 m.

The Puelches Formation is an Early Pliocene, sandy fluvial and eolian unit that constitutes the deepest and most transmissive aquifer in the MRAS. The lower section of the formation is mainly sandy and behaves as a confined aquifer, whereas the upper section is clayey and behaves as an aquitard (Auge, 1986, 2004). Within the MRB, the thickness of the Puelche Aquifer is 13 to 33 m and its transmissivity ranges from 200 to 800 m²/d (IHLLA, 2011). The aquitard is formed by silty and clayey layers with a variable joint thickness of few decimeters to almost 40 m and with hydraulic conductivities around $6 \cdot 10^{-5}$ m/d (Fili et al., 1999; IHLLA, 2011, 2012). The aquitard is considered a unit of the MRAS. Though it is not continuous across the MRB, it is broadly extended and tends to thicken to the SW. The clayey layers appear at 14–15 m depth to the NE of the MRB, and at 63–77 m to the SW (Mancino et al., 2013).

The youngest geological units are the Pampeano (Pleistocene-Holocene), and Postpampeano (Holocene) sediments, and together constitute the Upper Aquifer in this work. Their transmissivity ranges 60 to 200 m²/day (IHLLA, 2012). The Pampeano Sediments consist of fluvial and lacustrine clayey to sandy silts, eolian loess of volcanic origin, with the presence of petrocalcic layers. Its mineralogy consists of

plagioclase, quartz, K-feldspar, volcanic glass, calcite, opal, mica, and some contents of heavy minerals (magnetite, titanite, ilmenite). Pyroxene and amphibole are less abundant, while montmorillonite and illite dominate the clay size fraction (Teruggi, 1957; González Bonorino, 1965; Martínez et al., 1998; Tófaló et al., 2005; Bonorino et al., 2008). The Postpampeano Sediments are alluvial, lacustrine, marshy and eolian sandy silt, silty loam, with hard carbonate crust layers and disseminated carbonate dust (Panarello et al., 1995).

The regional groundwater flow is from SE to NW in the two aquifers (Fig. 2), and their piezometric surfaces are closely similar, suggesting an important hydraulic connection between them. This is consistent with the hypothesis of generalized recharge from the Upper to the Puelche aquifers stated by many authors (Auge, 2004; Vives et al., 2012; IHLLA, 2012), which is supported by the discontinuous spatial extent and the heterogeneity of the aquitard. On the other hand, the phreatic aquifer is strongly influenced by the abundant shallow surface water bodies existing in the MRB (Matanza-Riachuelo River, small streams and lagoons; UNLP, 2010; IHLLA, 2012).

3. Material and methods

3.1. Data used

This work is based on the study of hydrochemical and isotopic data of groundwater samples from the Upper and the Puelche aquifers. A total of 69 groundwater samples were taken in March–April 2014 in the ACUMAR's groundwater monitoring network (Fig. 1). They were collected from 35 and 34 boreholes penetrating the top of Upper and Puelche aquifers and the bottom of the last, respectively (Fig. 1). For an easier reading of this text, the symbols of the electric charges have been omitted.

3.2. Chemical and isotopic analyses

Major chemical components (Cl, SO₄, Na, K, Ca, Mg), and some minor and trace ones (NO₃, PO₄, F and As), were analyzed at the laboratory of the Argentina's National Water Institute (INA in its Spanish initials) by standard methods (see APHA et al., 2005). Electrical conductivity (EC), pH and alkalinity (quoted in this paper as equivalent HCO₃) were measured both on-site and at the INA's laboratory also by standard methods. The quality of the chemical analyses was evaluated combining three criteria: (1) a ionic balance error $\leq 10\%$; (2) the ratio of EC (in $\mu\text{S}/\text{cm}$) with respect to the sum of cations and anions (in meq/L), that should have values between 80 and 100, and (3) the relationships between EC values and the concentrations of individual solutes, which usually follow well defined patterns. Most of the chemical analyses (75%) showed ionic balance errors smaller than 10%, whereas the remaining 25% (analyses of samples 2F, 9F, 11F, 24F, 25F, 32F, 10P, 6F, 8F, 13F, 14F, 14P, 18F and 21F) showed errors slightly higher (Fig. 2).

The stable isotopes of water (²H and ¹⁸O) were measured in all the samples. The analyses were carried out by laser spectroscopy at the Isotope Hydrology Laboratory of the Institute of Quaternary and Coastal Geology (National University of Mar del Plata, UNdMP, Argentina). Deviation values (δ) were reported in ‰ after the Vienna Standard (V-SMOW); the reported analytical errors are $\delta^{18}\text{O}$: $\pm 0.3\%$ and $\delta^2\text{H}$: $\pm 0.2\%$.

3.3. Methods used to identify the main hydrogeochemical and mixing processes

The hydrochemical and isotopic data were studied using a multi-tool approach. Main groundwater chemical facies and evolution trends of both the Upper and Puelche aquifers were identified using the classical Piper diagram (Fig. 3). Bivariate analyses were performed in order to identify the main hydrogeochemical and physical processes responsible for the spatial distribution and evolution of the groundwater chemistry.

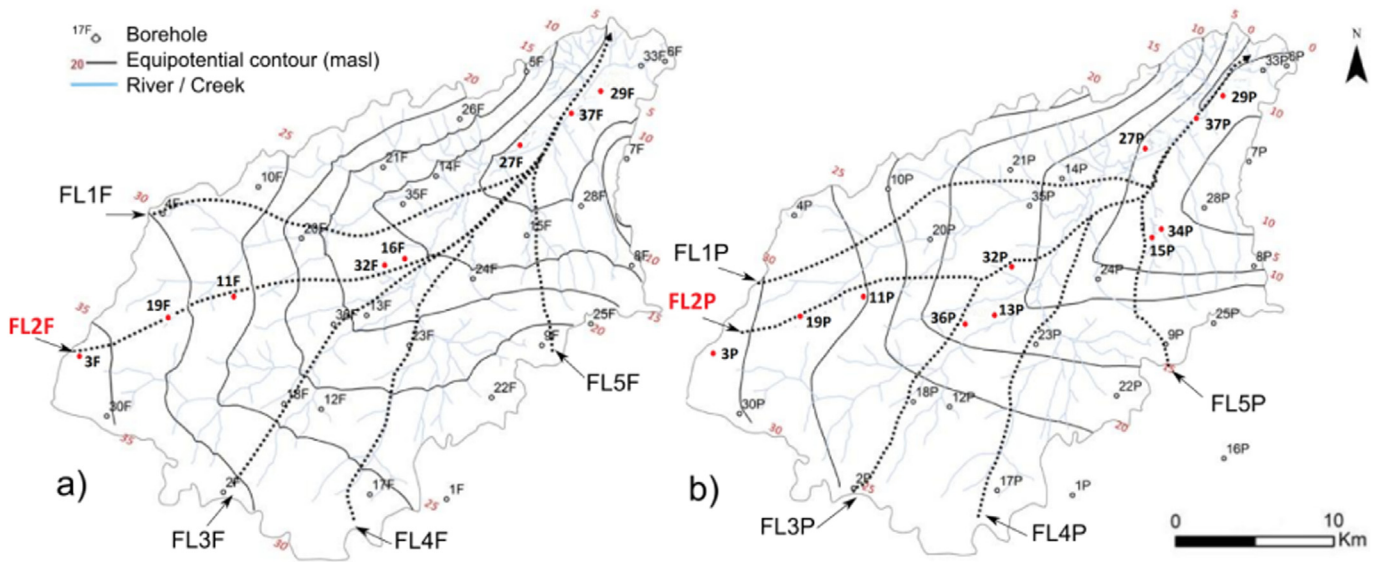


Fig. 2. Piezometric surfaces in December 2012, borehole location, and main regional flow paths used for the hydrogeochemical study of a) the Upper Aquifer, b) the Puelche Aquifer. (Modified from Melián, 2014.)

Excesses of Na + K with respect to Cl contents and deficit of Ca + Mg with respect to HCO₃ + SO₄ contents allowed confirming the occurrence of cation exchange (Fig. 4). The comparison of stable isotope values and Cl contents, and of major ion and electrical conductivity (EC) values, helped determine the expected evolution of the mixing of typical average fresh water of each aquifer and standard sea water, and the occurrence of other processes such as evapotranspiration (Figs. 5 and 6). The occurrence of mineral dissolution and precipitation processes was assessed through the study and modeling of saturation indices (SI) with PHREEQC (Parkhurst and Appelo, 2013) using temperature, pH and alkalinity data measured on site (Fig. 7). The existence of several sources of SO₄ in both aquifers was studied using Ca/SO₄, NO₃/SO₄ and SO₄/Cl ratios (in meq/L) together with

SI (Fig. 8). The probable location of those sources was studied through the analysis of regional trends for SO₄ and Cl contents, and for SO₄/Cl and Na/Cl ratios (in meq/L), in samples from the top and the bottom of the Puelche Aquifer according to the borehole location within the basin (Fig. 9). Major chemical trends existing along regional flow paths in the two main aquifers were identified based on piezometric maps from December 2012 (Fig. 10). In this paper, only one flow path in each aquifer is described (FL_{2F} and FL_{2P} flow path lines in Fig. 2, for the Upper and the Puelche aquifers respectively). FL_{2F} and FL_{2P} resume the major groundwater processes taking place in this groundwater system as a whole and in each aquifer separately. In order to increase the available amount of data for each flow path, data from nearest boreholes were also used.

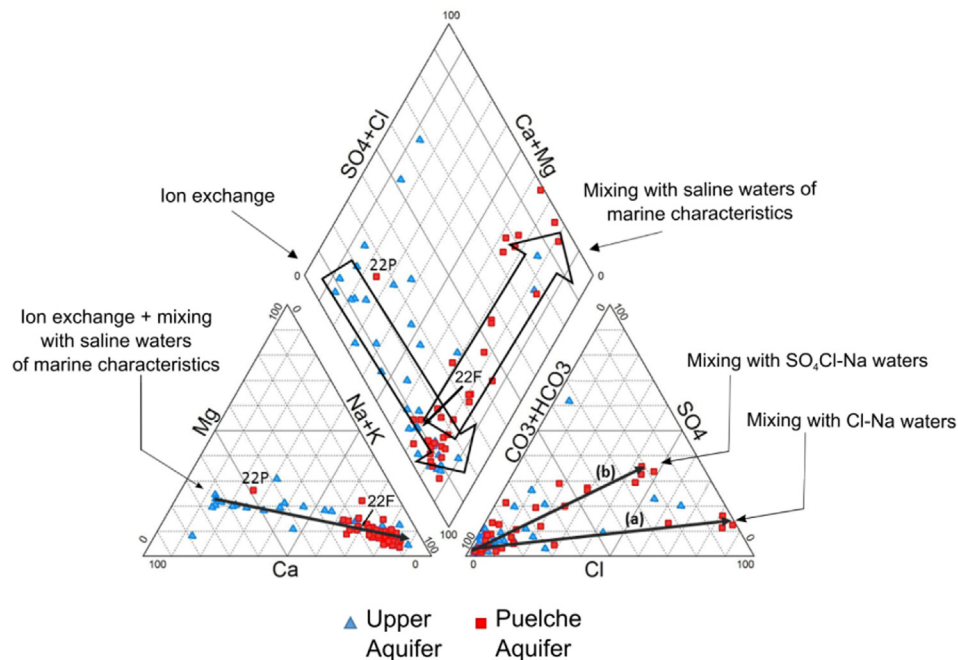


Fig. 3. Projection on a Piper diagram of the major chemical components of groundwater samples from the Upper and Puelche aquifers. Arrows highlight the main trends observed, whose causes are discussed in the text.

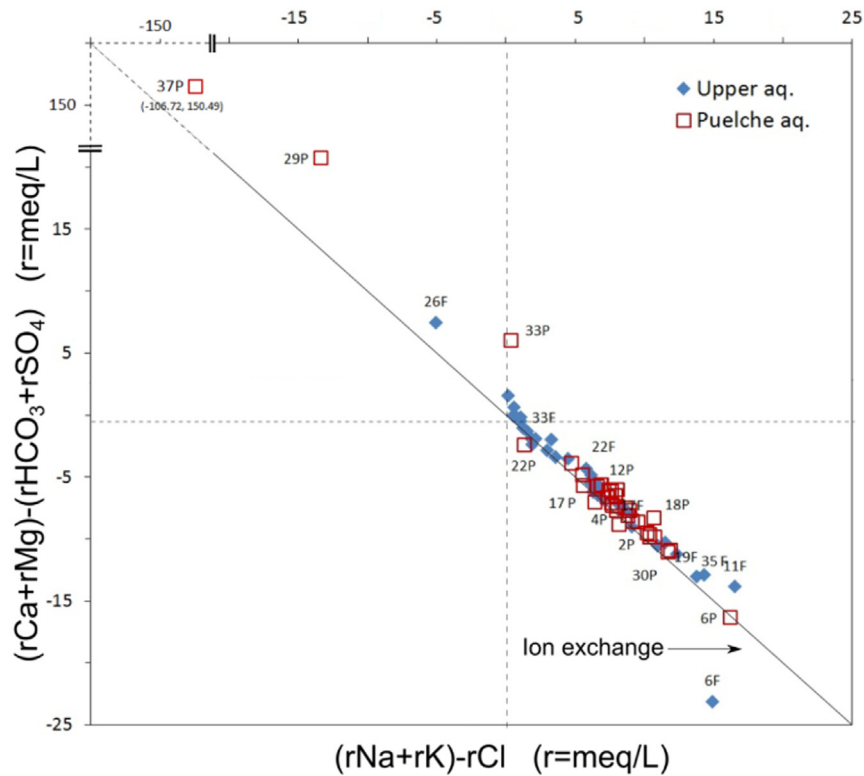


Fig. 4. Comparison of the Na + K excesses with respect to Cl contents and the Ca + Mg deficit with respect to $\text{HCO}_3 + \text{SO}_4$ contents (in meq/L) to assess the occurrence of cation exchange in the Matanza Riachuelo Aquifer System. In most samples the magnitude of Na + K excess is similar to that of Ca + Mg deficit, supporting the hypothesis that cation exchange is one of the major processes controlling groundwater composition in the studied system. See more details in the text.

3.4. Hydrogeochemical modeling approach

The physical and hydrogeochemical processes deduced using the multi-tool approach described in the former section generated a hydrogeochemical conceptual model of the main processes controlling the chemical facies in the MRAS and their regional distribution. The main features of the hydrogeochemical conceptual model were validated through modeling with PHREEQC. Two models were performed: Model 1 (M1) tries to explain the evolution of the most common water type at the MRAS, the Na- HCO_3 water, from the initial recently recharged or recharging Ca- HCO_3 water (see Section 4.3.1). Model 2 is devoted to the understanding of the groundwater chemistry evolution that involves the mixing between a Na- HCO_3 groundwater and sea water (see Section 4.3.2).

4. Results

4.1. Identification of main hydrogeochemical processes

The hydrochemical data projected in a Piper diagram (Fig. 3) revealed that in the MRAS there are two main chemical facies, Ca- HCO_3 and Na- HCO_3 , and two less abundant facies, Na-Cl and Na- ClSO_4 . All the chemical types are related by three main evolution trends, which tell about the most important physical and hydrogeochemical processes occurring in the MRAS. Many samples in the Upper Aquifer are of the Ca- HCO_3 type, which suggests that this should be the composition of newly recharged groundwater. This facies points to the occurrence of processes that dissolve carbon during groundwater recharge. In fact, the dominance of HCO_3 among the anionic content in most of the samples can be explained by several processes supported by the mineralogy of the Pampeano and Postpampeano sediments: dissolution of soil CO_2 , of carbonate minerals (calcite, magnesian calcite and/or dolomite), and of albite and anorthite.

A first trend shows the transformation of Ca- HCO_3 waters into Na- HCO_3 by a progressive increment of the Na contents, which becomes the main cation in most of the samples (Fig. 3, cations triangle) while HCO_3 remains as the main anion (Fig. 3, anions triangle). This is the result of a cation exchange process with Na release and Ca (and may be Mg) uptake. A second trend observed shows an increment of Cl contents, until it becomes the dominant anion, in some samples in which Na remains the dominant cation (Fig. 3, line (a) in the anions triangle). This is the result of mixing between Na- HCO_3 type water and typical Na-Cl sea water. Lastly, a third trend shows that in many samples the SO_4 concentrations increase more than expected from the mixing with sea water (Fig. 3, line (b) in the anions triangle), suggesting the existence of other processes (and sources of sulfate) introducing SO_4 in solution. Those general observations support the hypothesis that the labels of samples 22P and 22F were exchanged, most probably during the sampling survey.

The feasibility of the physical and hydrogeochemical processes deduced above has been assessed using different techniques, and it is the focus of the following sections.

4.1.1. On the occurrence of cation exchange

The occurrence of this process has been assessed by means of solute mass balances and hydrogeochemical modeling. Fig. 4 shows the excesses of Na + K contents with respect to Cl contents, compared to the excesses of Ca + Mg with respect to $\text{SO}_4 + \text{HCO}_3$ contents (all of them in meq/L). Most of the samples show a notable excess of Na + K with respect to Cl which is balanced by the deficit of Ca + Mg with respect to $\text{HCO}_3 + \text{SO}_4$. This means that cation exchange with Na release and Ca + Mg uptake is one of the main hydrogeochemical processes controlling groundwater composition in the MRAS. However, the samples 37P, 29P and 26F show deficit of Na and excess of Ca + Mg, which means that they are affected by a cation exchange process of Na uptake and Ca and/or Mg release. This is the most usual exchange process in aquifers under active salinization by marine water, which is

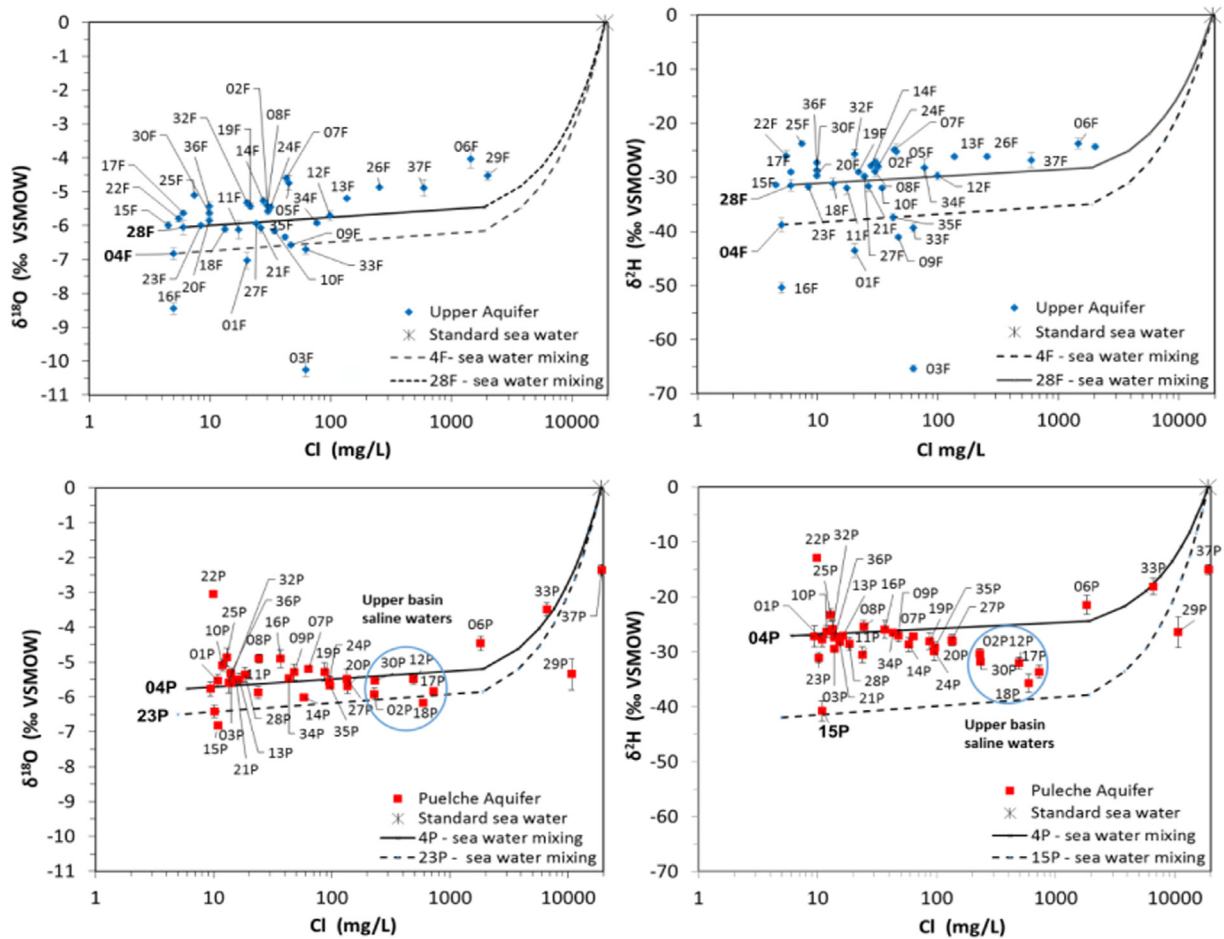


Fig. 5. Stable isotopes deviations ($\delta^{18}\text{O}$, $\delta^2\text{H}$ ‰ VSMOW) and Cl contents (mg/L) of groundwater samples from the Upper and Puelche aquifers. Solid lines represent the expected evolution for mixing of typical average fresh water of each aquifer and standard sea water; dashed lines represent the expected evolution for mixing between sea water and some of the isotopically lightest samples measured in each aquifer. The samples circled are from the Puelche Aquifer in the upper basin, where sea water has a different origin than in the lower basin (see more details in the text).

consistent with the fact that the three samples (which are from the lower basin) have variable contributions of sea water. Moreover, these three samples plus sample 33P fall above the unity-slope line, showing larger Ca + Mg excesses with respect to $\text{HCO}_3 + \text{SO}_4$ than the expected if the four components had the same mineral sources (gypsum, calcite and dolomite). This suggests that in the lower basin, and probably not at a broad scale, in addition to cation exchange and dissolution of carbonate minerals and may be of gypsum, some other hydrogeochemical processes are either incorporating Ca and/or Mg to groundwater or uptaking HCO_3 and/or SO_4 . Considering the fact that sedimentary organic matter is abundant in the lower basin, the most plausible process to explain the observed imbalance is sulfate reduction.

Oppositely, sample 6F falls below the unity-slope line, suggesting in this case the existence of processes incorporating HCO_3 and/or SO_4 to groundwater from sources different to carbonate minerals and gypsum. The mineralogy of the aquifer allows considering two processes as the most probable: the solubilization of carbon from degrading sedimentary organic matter, and of sulfur from the oxidation of reduced sulfur species (sulfides). The feasibility of these processes is discussed in Section 4.1.4.

4.1.2. On the occurrence of fresh water and sea water mixing

The occurrence of fresh groundwater mixing with sea water was first assessed comparing the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values with the Cl contents (Fig. 5). The isotopic values range from -10.26‰ to -2.36‰ for $\delta^{18}\text{O}$, and from -65.3‰ to -12.9‰ for $\delta^2\text{H}$, whereas Cl concentrations range from 5 mg/L to 19,210 mg/L. The Cl contents vary from values

typical of rain water to those typical of sea water, and in most of the samples the isotopic composition falls close to a theoretical mixing line between common isotopic fresh water values found in the Upper and Puelche aquifers (average values roughly around -6.0‰ for $\delta^{18}\text{O}$ and -30‰ for $\delta^2\text{H}$ in the Upper Aquifer, and -5.7‰ for $\delta^{18}\text{O}$ and -27‰ for $\delta^2\text{H}$ in the Puelche Aquifer) and standard sea water ($\delta^{18}\text{O}$ and $\delta^2\text{H} = 0\text{‰}$). The notable dispersion of isotopic values in the fresh water component, which amounts some $\pm 0.5\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 5\text{‰}$ for $\delta^2\text{H}$, is assumed to be the result of the regionally variable evaporation process (Gibson et al., 1993; Mayr et al., 2007). Fig. 5 represents two hypothetical mixing lines: solid lines are theoretical mixing lines with a fresh water component having the most frequent isotopic values of each aquifer (represented by samples 28F in the Upper Aquifer and 04P in the Puelche Aquifer); dashed lines represent theoretical mixing lines with some of the lightest fresh water components in each aquifer (represented by samples 04F in the Upper Aquifer and 15P in the Puelche Aquifer). A few samples in the Upper Aquifer (e.g. 116F, 03F, 01F) have unexpectedly light values which cannot be easily explained; they may represent particular rain events not evaporated. Several authors find the same situation, for example Ingraham and Taylor (1991) and Rozanski et al. (1993). They are lighter than the average rain water in Buenos Aires city characterized by Dapeña and Panarello (2004) ($\delta^{18}\text{O} = -5.5\text{‰}$, $\delta^2\text{H} = -30\text{‰}$).

The fact that groundwater in the Puelche Aquifer resembles the Cl and isotopic values and even the dispersion found in the Upper Aquifer supports the hypothesis that the first aquifer is recharged by the second one, and suggests that vertical transfer is rapid. However, this has yet to

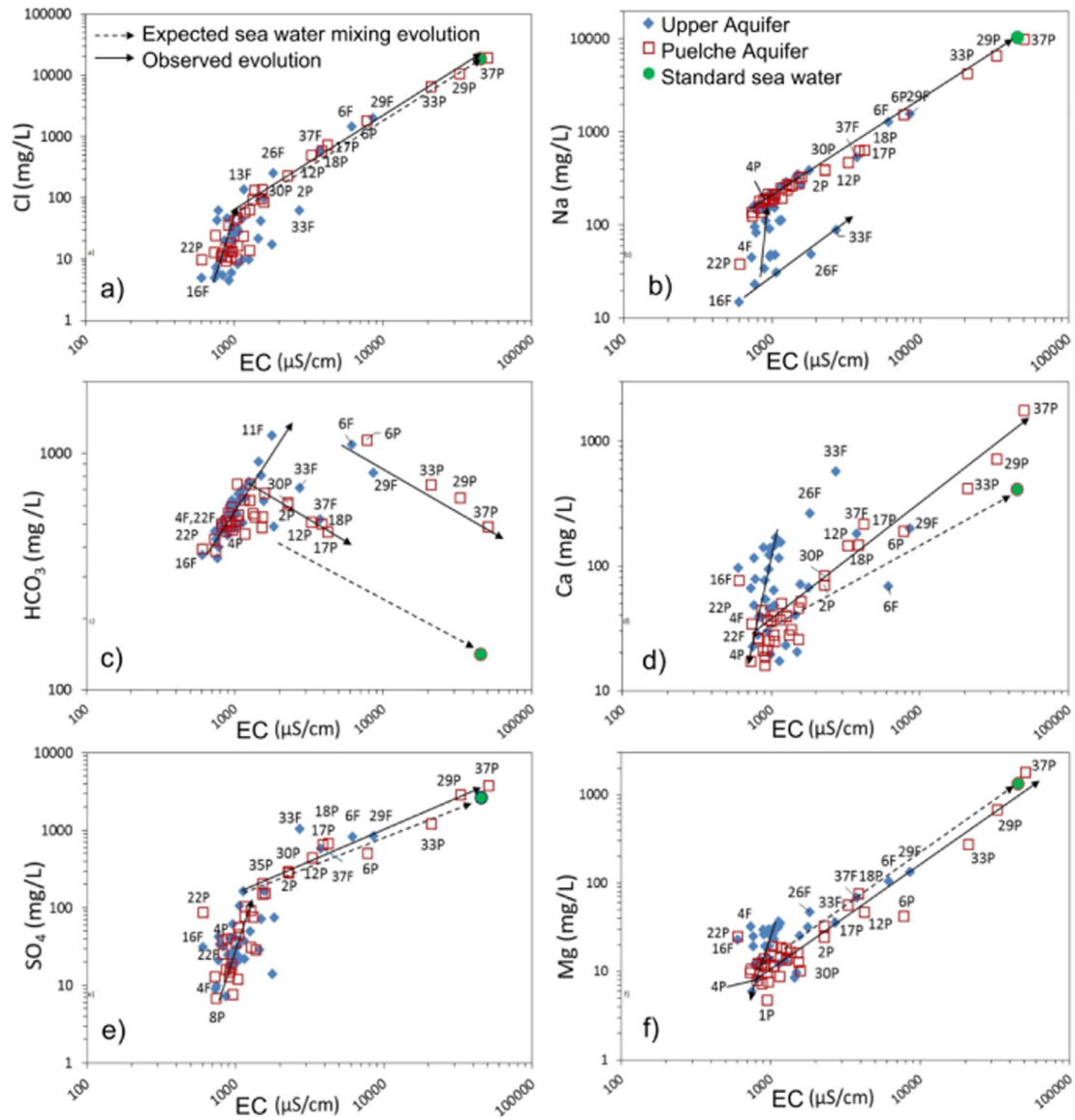


Fig. 6. Major ion concentrations (mg/L) and electrical conductivity (EC, $\mu\text{S}/\text{cm}$) in the groundwater samples collected in the Upper and Puelche aquifers. Standard sea water composition is shown with a green circle. Dashed lines show the theoretical conservative mixing trends between typical fresh groundwater in both aquifers and sea water, whereas solid lines show the real observed evolution trends. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

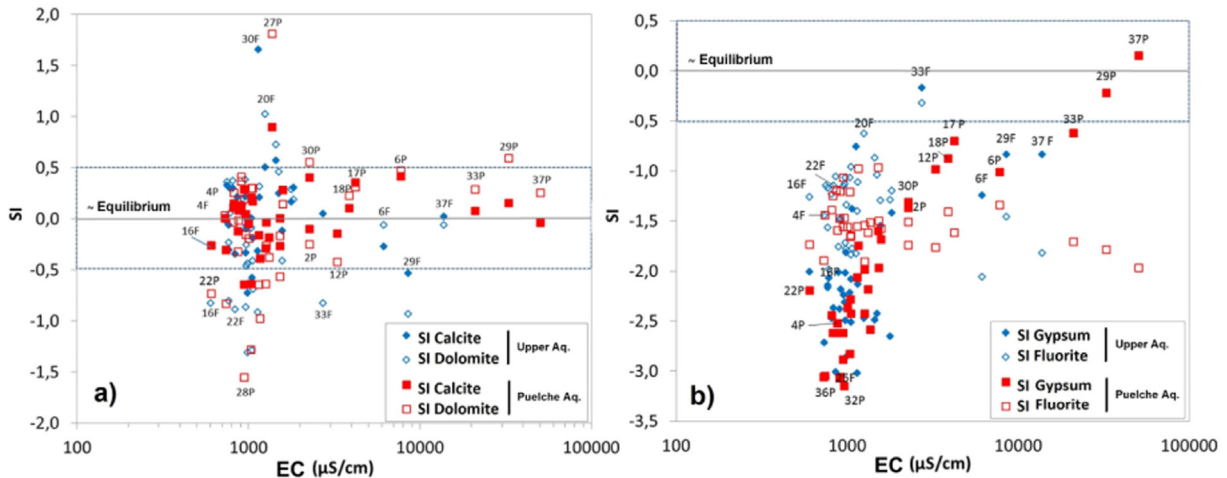


Fig. 7. Mineral saturation indices (SI) and electrical conductivity (EC, $\mu\text{S}/\text{cm}$) in groundwater samples from the Upper and Puelche aquifers. a) Calcite and dolomite. b) Fluorite and gypsum.

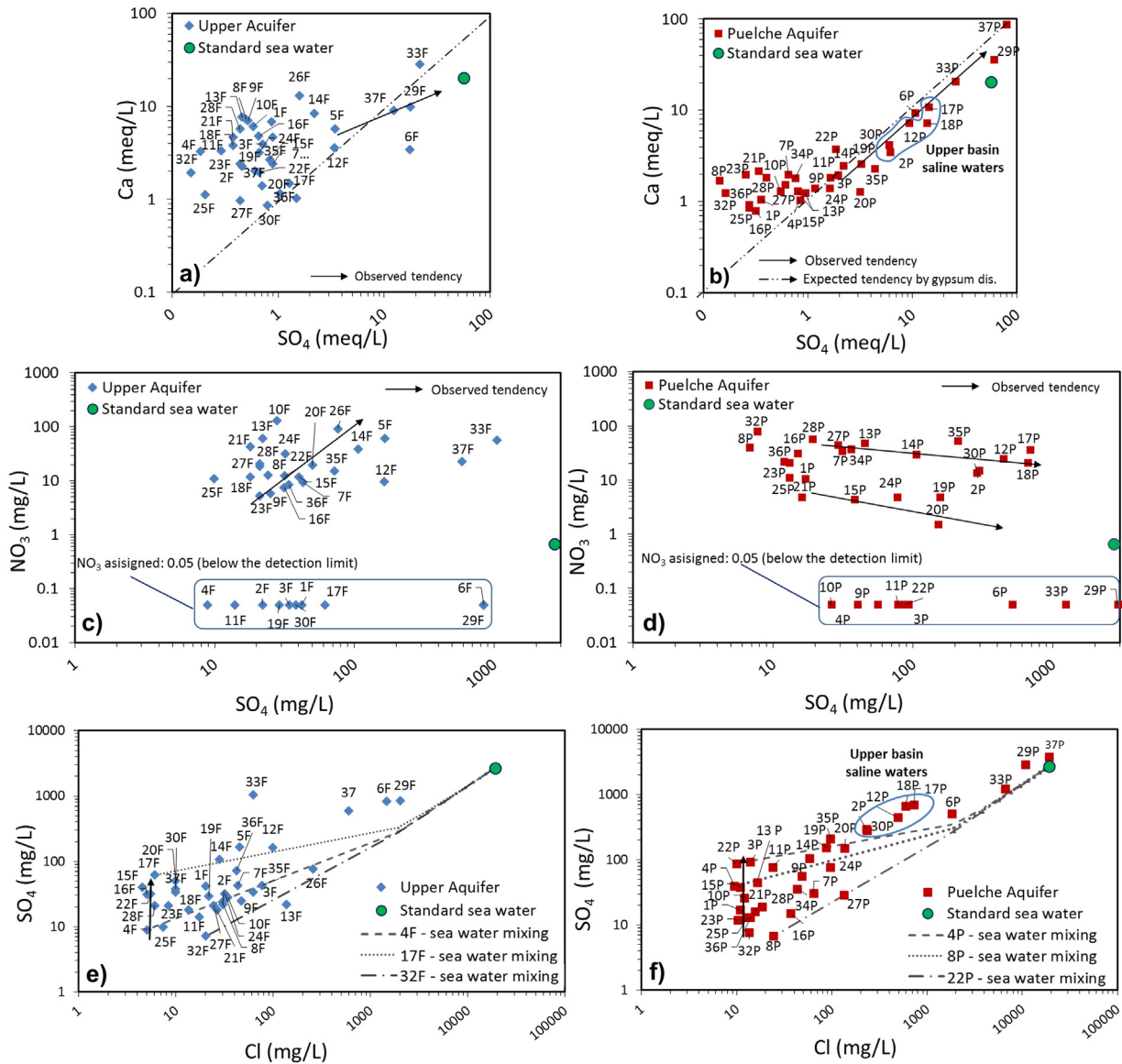


Fig. 8. a) Relationship between SO₄ Ca contents (meq/L), and expected trend for gypsum dissolution, in groundwater samples of the Upper aquifer; b) idem for the Puelche Aquifer. c) Relationship between SO₄ and NO₃ (mg/L) at the Upper Aquifer and observed trends; d) idem at the Puelche Aquifer. e) Relationship between Cl and SO₄ (mg/L) contents in the Upper Aquifer and theoretical conservative mixing trends between standard sea water and different samples representative of fresh water in the aquifer; f) idem for the Puelche Aquifer.

be confirmed. The same situation would be observed if the samples that theoretically represent the Puelche Aquifer were mixtures of water from both aquifers (diverse possible causes may produce mixtures, for example a deficient isolation of the boreholes).

Beside this, there is a set of samples in the Puelche Aquifer whose lighter-than-average isotopic values may obey to a different reason than the proposed for the Upper Aquifer. They are samples 02P, 12P, 17P 18P and 30P (circled in Fig. 5) and come from boreholes in the upper basin. Their salinity cannot be explained by mixing with sea water encroached in the distant lower basin, but it can obey to mixing with connate marine water present in the upper clayey sediments of the underlying Paraná Formation. The geological structure in this zone supports this hypothesis, as the top of the Paraná Formation is just a few meters under the bottom end of the boreholes (Mancino et al., 2013). Moreover, the isotopic values of these samples suggest that their freshwater component is somewhat lighter than the average present day recharge to the Upper Aquifer. This cannot obey to recharge at higher locations, as the MRB is within the Pampa plain and the closest mountain area (Tandilia Range, <300 m asl) is >300 km to the S, so the cause must be another -yet unknown-. Finally, samples 29P and

37P in the lower basin also seem to have a fresh water component lighter than present day local recharge.

The occurrence of fresh groundwater mixing with sea water was also checked studying the relationship between ionic concentrations and EC (Fig. 6). Most of the more mineralized groundwater samples in the two aquifers evolve as expected for a mixing between fresh local groundwater and sea water. This is particularly clear for Cl, Na, Mg, Ca, and SO₄ (Fig. 6a–d and f). Also as expected, some samples show deviations from the conservative mixing line that can be explained by hydro-geochemical processes, especially for HCO₃, Ca, Mg and SO₄ (Fig. 6c–e and f). In the less mineralized waters, HCO₃ concentrations increase much more (in relative terms) than Cl (Fig. 6c), which suggest that in addition to evaporation there are other causes to explain the increase of alkalinity. They can be calcite and/or dolomite dissolution, which would supply also Ca and Mg to groundwater, though they disappear by exchange with Na. In the samples affected by mixing with sea water, HCO₃ decreases as a result of calcite solubility constraints in the mixtures.

In the most mineralized samples of both aquifers, SO₄ concentrations evolve as expected for mixing with sea water. But at least samples

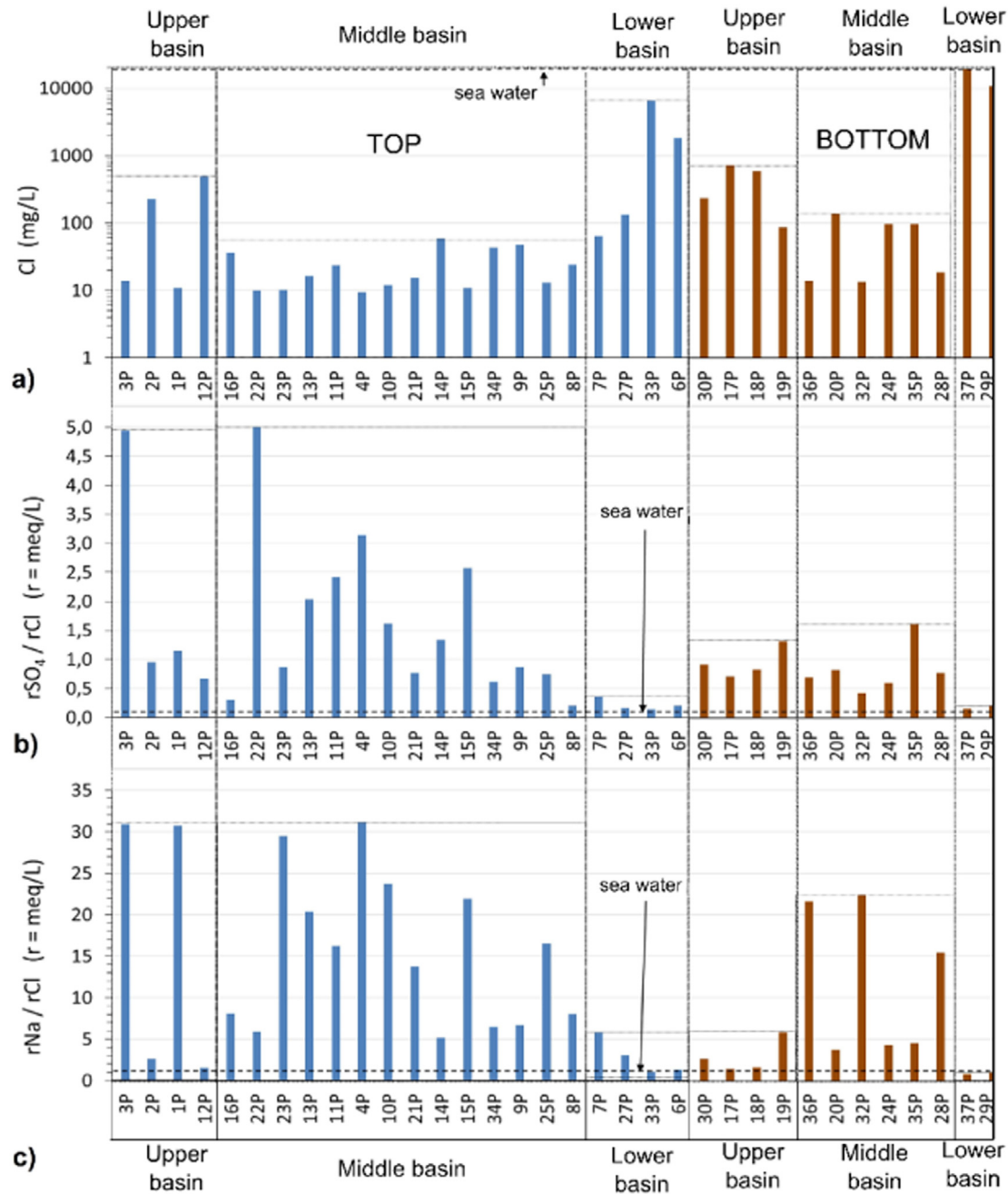


Fig. 9. a) Cl content (mg/L), b) SO_4/Cl ratio values (meq/L) and c) Na/Cl ratio values (meq/L) in samples from the top and the bottom of Puelche Aquifer according to borehole's location within the basin. Dashed lines indicate typical values in sea water; continuous lines indicate maximum values measured.

33F (Upper Aquifer), 29P and 37P (Puelche Aquifer) in the lower basin, and samples 17P and 18P (Puelche Aquifer) in the upper basin, have more SO_4 than expected from this process. This remarks the existence of additional SO_4 sources and processes than mixing with sea water. This subject is addressed with detail in Section 4.1.4.

Fig. 6 provides a further insight into the existence of mixing. Apparently, in fresh water of the Upper Aquifer without sea water contribution the contents of the major solutes increase around one order of magnitude, while EC increases less significantly, between $\approx 700 \mu S/cm$ and $\approx 1000 \mu S/cm$. This is assumed to be mostly the result of evapotranspiration. However, a detailed study of the Na, Ca and Mg graphs show that while Na contents increase with increasing EC, Ca and Mg contents in reality decrease. This is a result of the dominant cation exchange process deduced in Section 4.1.1, and means that

cation exchange contributes more significantly than any other hydrogeochemical or physical process to the concentrations of Ca and Mg of fresh groundwater in the most abundant $Na-HCO_3$ water type of the MRAS.

Another relevant information obtained from Fig. 6 refers to the location where the relevant cation exchange process takes place within the groundwater flow network of the MRAS. Fig. 6b, d and f show that the less mineralized waters in the Upper Aquifer have lower Na contents and major Ca and Mg contents than the less mineralized waters in the Puelche Aquifer. In fact, the contents of Na, Ca and Mg in the less mineralized samples of the Puelche Aquifer are similar to those of the fresh groundwater in the Upper Aquifer most modified by cation exchange. This means that the preminent cation exchange process takes place mainly in the Upper Aquifer.

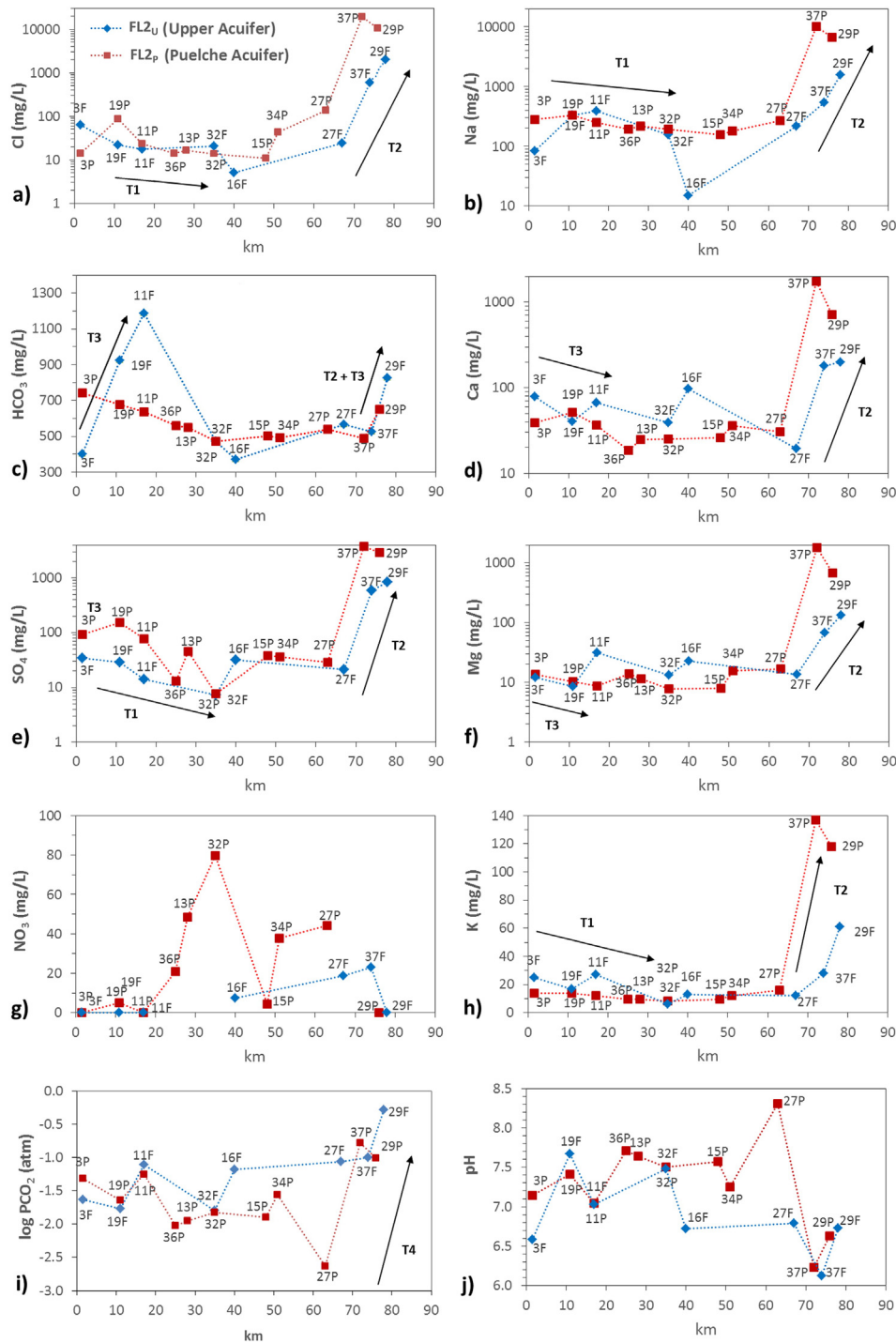


Fig. 10. Spatial evolution of Cl, Na, HCO_3 , Ca, SO_4 , Mg, NO_3 and K content (mg/L), and of pH values, along flow paths FL2 in the Upper and the Puelche aquifers (see Fig. 2). The observed evolution trends tagged with arrows are discussed in the text.

4.1.3. On the occurrence of mineral dissolution

Mineral saturation indices (SI) of calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), fluorite (CaF_2), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) were calculated to contrast the hypothesis that mineral dissolution could contribute to the increase of HCO_3 , Ca, Mg and SO_4 concentrations in fresh groundwaters (Fig. 7). Assuming equilibrium for SI within ± 0.5 , most of the groundwater samples in both aquifers are in equilibrium with calcite and dolomite, including most of the less mineralized samples (Fig. 7a). Only a few samples from both aquifers are clearly subsaturated with respect to dolomite and a couple of them with respect to calcite, independently

of their location within the basin (Fig. 7a). On the other hand, only a few samples are oversaturated in calcite or dolomite: sample 20F (Upper Aquifer, middle basin) is oversaturated in calcite; samples 30F (Upper Aquifer, upper basin), and 27P (Puelche Aquifer, lower basin) are oversaturated in dolomite. Most of the samples from both aquifers are subsaturated in gypsum and fluorite (Fig. 7b), except samples 33F (Upper Aquifer), 29P and 37P (Puelche Aquifer). The last three samples are high mineralized waters from boreholes located in the lower part of the basin.

Given that most of the groundwater in the MRAS are close to equilibrium for calcite and dolomite and subsaturated for gypsum and fluorite,

it could be concluded that only the dissolution of the two last minerals can be expected. However, it is important to consider two things: rain water - which is the source water for recharge to the Upper Aquifer - is strongly subsaturated in all minerals, and carbonated minerals (mostly calcite) are abundant in the geological formations in the Upper Aquifer. Thus, calcite dissolution must take place at least during infiltration due to the subsaturation of recharge water, though calcite saturation is probably achieved shortly after infiltration. Moreover, the widespread occurrence of cation exchange with Ca and Mg uptake into the solid surfaces of clay minerals is probably inducing calcite subsaturation and dissolution, even if this process occurs at very local scale near the minerals surfaces.

4.1.4. Assessing sulfate sources

In order to identify the SO_4 sources and dissolution processes existing in the MRAS, four potential plausible processes were evaluated, even if no direct information is available from some of them: (1) gypsum dissolution, (2) agricultural or sewage contamination, (3) mixing with sea water, and (4) oxidation of sulfide minerals. The relationships between SO_4 and Cl, Ca and NO_3 were studied to assess common trends that could obey to common sources and processes.

As regards to gypsum dissolution as a potential SO_4 source, even if in this study mineralogical analyses have not been performed, the existence of gypsum is quite common in coastal sedimentary systems like the MRB. Moreover, other authors (Logan and Nicholson, 1998; Logan et al., 1999) mention the existence of gypsum in the Puelches Formation in La Plata coastal aquifer system, not far and to the East of the MRAS. As was exposed in Section 4.1.3, most of the groundwater samples (except samples 33F, 29P and 37P) are subsaturated with respect to gypsum, thus if this mineral is present it can dissolve. The possible occurrence of gypsum dissolution is assessed with Fig. 8a and b. They show that most of the samples from the two aquifers have SO_4 contents <1 meq/L, and probably their SO_4 contents are just the result of evapotranspirative concentration of the atmospheric supply. But gypsum dissolution cannot be discarded in: (1) groundwater samples of both aquifers with moderate SO_4 contents ($1 < \text{SO}_4 < 10$ meq/L); (2) in samples from the Puelche Aquifer in the upper part of the basin showing large SO_4 contents ($\text{SO}_4 > 10$ meq/L) and SO_4/Ca ratios close to 1 (2P, 12P, 17P, 18P and 30P), and (3) in sample 37P of the Puelche Aquifer in the lower basin. This sample is, in practice, sea water somewhat modified by specific hydrogeochemical processes.

Even not being particularly intense activities, agriculture and cattle rising are widespread performed in the MRB. On the other hand, sewage coverage in the basin is <50%. The possibility of agricultural and/or sewage pollution as potential SO_4 sources was studied through the SO_4 - NO_3 relationship (Fig. 8c and d). Although in some samples from the Upper Aquifer there is a positive correlation between SO_4 and NO_3 contents, the trend is not clear, but some contribution cannot not be discarded. On the other hand, in the Puelche Aquifer NO_3 decreases as SO_4 increases, pointing out that the main source of SO_4 in this aquifer is not related with pollution. Thus, although some contribution of SO_4 from the mentioned pollution sources cannot be discarded, they do not seem to be quantitatively significant, at least at regional scale.

With respect to the contribution of SO_4 from sea water, as was discussed in Section 4.1.2 SO_4 and Cl contents in the most mineralized samples fall close to the theoretical mixing lines between fresh groundwater and sea water. Moreover, Fig. 8e and f shows that mixing with sea water can explain the SO_4 contents observed in most of the samples. Thus, sea water is clearly a significant source of SO_4 for the saline samples. But Fig. 8e and f also shows that some brackish samples of the Puelche Aquifer in the upper part of the basin (2P, 30P, 12P, 17P and 18P) and some samples of the Upper Aquifer in the lower part of the basin (6F, 29F, 33F and 37F) have higher SO_4 contents than expected from mixing with sea water, which points to the contribution of mineral sources. Also samples 29F, 37F (Upper Aquifer), 29P and 33P (Puelche Aquifer) in the lower part of the basin show

larger SO_4 contents than expected from mixing. All these samples may have sulfate contribution from gypsum, and may be also from sulfide oxidation, though the mineralogical data available are insufficient to verify these hypotheses.

On the other hand, as described in Section 4.1.2 the less mineralized samples from both aquifers show increasing SO_4 content with increasing EC. In a first approach, this can be assumed to be the effect of evapotranspiration. However, evapotranspiration makes the Cl contents to increase 100 times (from <10 mg/L to ≈ 100 mg/L), while SO_4 contents increase around 200 times (from <10 mg/L to ≈ 200 mg/L). This is more clearly assessed by Fig. 8e and f: vertical upward arrows indicate that in the less saline samples (Cl < 5 mg/L in the Upper Aquifer and <20 mg/L in the Puelche Aquifer) SO_4 increases from 7 to 8 mg/L up to 80–100 mg/L, while Cl remains stable. These observations suggest that the increase of SO_4 observed in the less saline waters is the combined result of evapotranspiration and dissolution of some mineral source, most probably gypsum and/or sulfides. On the other hand, the figures also show that mixing with sea water affects to fresh water samples with very different SO_4 contents, suggesting that the deduced mineral dissolution process takes place on a local basis. This is consistent with the usual spatial distribution pattern of secondary gypsum and sulfides in coastal sedimentary formations, even though the presence of these minerals in the MRB has not been studied yet.

Besides the lack of adequate studies, there are insights that the last potential SO_4 source and process, sulfide oxidation, is a feasible process in the MRAS: pyrite traces have been found in RX diffractions performed on sediment samples from a deep borehole recently drilled in the lower basin, nearby the Río de La Plata coast line (own data not included in this work). Thus, hypothetically sulfide oxidation and solution (for example, due to piezometric drawdown induced by exploitation to the most used Puelche Aquifer) could contribute, alone or jointly with gypsum dissolution, to the SO_4 contents of samples from both aquifers around the basin, and most likely to samples with low to moderate SO_4 contents in the upper and middle parts of it.

Finally, for the Puelche Aquifer the most probable location of the deduced mineral dissolution process, in terms of X, Y and depth, was assessed studying the Cl contents and the SO_4/Cl and Na/Cl ionic ratios according to the location of samples across the basin and to their provenance from boreholes screened in the top or the bottom of the geological formation (Fig. 9). In general, Cl contents in the Puelche Aquifer tend to be higher in samples from the bottom of the aquifer (Cl ranges 12 to 19,200 mg/L), than those ones from the top of it (Cl ranges 5 to 2000 mg/L) (Fig. 9a). This is consistent with the formerly discussed hypothesis of sea water mixing and the different origins of sea water end-member at the lower and upper parts of the basin.

Brackish (Cl = 200 to 750 mg/L) samples 02P, 12P, 17P, 18P and 30P, from the Puelche Aquifer in the upper part of the basin, come from boreholes screened both at the bottom (30P, 17P and 18P) and at the top of the aquifer (boreholes 2P and 12P). Samples 12P, 17P and 18P have Na/Cl ratio values close to (in meq/L) of sea water (Na/Cl ≈ 1), while the other samples have values somewhat larger than sea water, but not larger than 2 (Fig. 9c). This supports the hypothesis of mixing with marine groundwater resident in the underlying Paraná Formation to explain the salinity of those samples.

Contrarily, the SO_4/Cl ratio (in meq/L) tend to have higher values in samples from the top of the Puelche Aquifer than in those from the bottom, thus suggesting a SO_4 source different to marine water from the Paraná Formation and located over the Puelche Aquifer, either in the aquitard layers (top of Puelches Formation) or in the Upper Aquifer (Pampeano Sediments). This source produces SO_4/Cl ratios far larger ($\text{SO}_4/\text{Cl} = 0.7$ to 1.4) than this of sea water ($\text{SO}_4/\text{Cl} \approx 0.11$), which points to gypsum and/or sulfide dissolution (Fig. 9b). Sulfide dissolution would require the availability of atmospheric oxygen in the pores of the aquitard layers at considerable depths (top of clays is at 40–50 m depth in the area; Mancino et al., 2013) and the oxidation of significant amounts of sulfides. While this is not impossible, the hydrodynamic

conditions in the upper basin (see Fig. 2) make it less probable than gypsum dissolution.

Finally, the most saline samples in the lower part of the basin taken both at the top (6P, 27P, 29P and 33P) and the bottom of the Puelche Aquifer (37P), have SO_4/Cl ratio values close to this of sea water, suggesting that mixing is the main source of SO_4 .

4.2. Spatial variability of groundwater composition along regional flow paths

The evolution of groundwater chemical composition was studied along different flow paths in the Upper and Puelche aquifers (Fig. 2). Among the five flow paths studied in each aquifer, only the flow paths FL2_F in the Upper Aquifer, and FL2_P in the Puelche Aquifer, are described here. FL2_F and FL2_P have almost the same route in both aquifers, which is useful to: (1) deduce the hypothetical hydraulic connectivity between both aquifers, and (2) identify the main processes affecting the spatial evolution of groundwater chemistry at regional scale.

The flow path FL2_F in the Upper Aquifer goes through the location of seven boreholes: 3F, 19F, 11F, 32F, 16F, 27F, 37F and 29F (Fig. 10). Three major chemical trends were identified. The first trend (T1) consists in a slight decrease of Cl, Na, SO_4 and K concentrations from the upper part (sample 3F) to the middle part (sample 16F) of the basin, displaying dilution downwards flow due to recharge to the unconfined aquifer of somewhat more saline groundwater coming from the upper basin. The increasing contribution of newly recharged water downwards flow is also reflected by the increasing NO_3 content (Fig. 10g). The second trend observed (T2) consists in a salinity increase in the lower part of the basin (samples 27F, 37F and 29F) (Fig. 10a–f and h). Those samples show a steep increase of major solute concentrations that induces a change of the chemical facies from Na- HCO_3 to Na-Cl type. This change was first identified in the Piper diagram (Fig. 3). Trend T2 is related with the already described mixing process of fresh groundwater and sea water in the lower part of the basin. The third trend observed (T3) consists in a notable increase of HCO_3 concentration and CO_2 partial pressure not accompanied by Ca and/or Mg increases. This is observed in the upper basin, between samples 3F, 19F and 11F (Fig. 10c and i). This evolution is assumed to reflect the incorporation to the saturated zone of newly recharged water with fresh CO_2 . The same type of trend can be observed in the lower part of the basin, between samples 37F and 29F. In this zone the oxidation of the sedimentary organic matter hosted into marine clay layers could be the main source of CO_2 and HCO_3 , as the soil surface is mostly paved and the samples are clearly in equilibrium with calcite and dolomite (see Fig. 7).

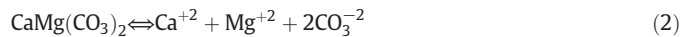
The flow path FL2_P in the Puelche Aquifer goes through the location of ten boreholes: 3P, 19P, 11P, 13P, 32P, 15P, 34P, 27P, 37P and 29P. Three major trends are also observed: T1, T2 and T3, which correspond to T1, T2 and T3 in flow path FL2_F (Fig. 10). The notable similarity of the evolution of the natural chemical components along flow in the two aquifers is consistent with the hypothesis of water transfer from the Upper to the Puelche Aquifer in most of the basin area.

4.3. Hydrogeochemical modeling

4.3.1. Model 1 (M1). Evolution of fresh Ca- HCO_3 water to fresh Na- HCO_3 water

Because most of the groundwater samples are currently in equilibrium with calcite (implying low capacity to dissolve this mineral), this model is based on the assumption that calcite and edaphic CO_2 dissolution from loess sediments would generate a Ca- HCO_3 groundwater type when the recharge process is fast. When recharge is slow or long transit times into the vadose zone are expected, cation exchange could be an important process in the groundwater evolution from Ca- HCO_3 to Na- HCO_3 type. Firstly, mass balances including the aforementioned geochemical processes were applied between samples 16F and 35F, representative of the Ca- HCO_3 and Na- HCO_3 water types, respectively

(Table 1). The mass balance summarized in Table 1 indicates that the supposed evolution from a Ca- HCO_3 water type to a Na- HCO_3 results on an increase of Na, HCO_3 , pH and SI of calcite and dolomite, while Ca, Mg and CO_2 concentrations decrease. Note that the differences among cations could be explained by ion exchange, promoting calcite and dolomite dissolution as a consequence of the Ca and Mg uptake. The increase on HCO_3 and pH could be a consequence of the dissolution of edaphic CO_2 and promoted carbonate dissolution. The feasibility of this conceptual model was studied through inverse modeling. It includes the formation of cation exchange complexes, and dissolution of edaphic CO_2 , calcite and dolomite, according to the following reactions:

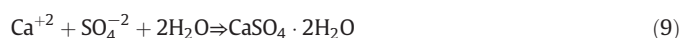
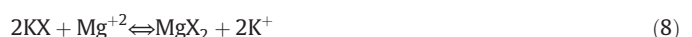
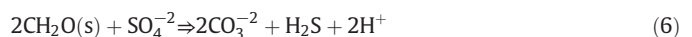


Inverse modeling results are summarized in Table 2. Two feasible models were obtained (M1a_inv and M1b_inv). Both ones predict a positive contribution for edaphic CO_2 and Na, and a negative contribution for Ca and Mg, due to ion exchange and edaphic CO_2 dissolution. Calcite and dolomite precipitates and dissolves, respectively, in M1a_inv, whereas only dolomite dissolution is predicted in M1b_inv. The thermodynamic feasibility of both models was assessed through direct modeling with PHREEQC, and their results are presented in Table 3 (M1a_dir and M1b_dir derived from M1a_inv and M1b_inv, respectively). Thus, both models predict solute concentrations close to those corresponding to sample 35F. However, the model including dolomite (M1a_dir) predicts low Mg concentration and dolomite SI in comparison with the real Na- HCO_3 water type.

4.3.2. Model 2 (M2). Mixing of fresh Na- HCO_3 groundwater and sea water

This model was devoted to the identification of the geochemical and mixing processes involved in the evolution of groundwater from a Na- HCO_3 to a Cl-Na type. In this case, the sample 33P was considered a result of mixing between two end-members: a lowly mineralized one, represented by sample 3P, and sea water, represented by sample 37P. Mixing proportions were calculated using Cl as a conservative tracer. The contribution of the low mineralized end-member was 65.5%, whereas the contribution of the saline one was 34.5%. Based on these mixing proportions, a theoretical water composition was calculated for comparison with the real sample (33P). Mass balance between real and theoretical mixed water is summarized in Fig. 11.

The mass balance between the real mix water (RMW) and theoretical mix water (TM) shows decrements in the SO_4 , HCO_3 , Ca and Mg contents, and increments in K and Na. In this case, the conceptual model is based on the same reactions than the previous model plus the following reactions:



In spite of the fact the Na concentrations are controlled by cation exchange according to Reactions (4) and (5), they are mainly affected by mixing (Fig. 11a). On the other hand, SO_4 concentrations decrease as a

Table 1

Chemical composition of samples 16F and 35F, located on a conceptual flow path, and mass balance between the downwards sample (35F, Na-HCO₃ type) and the upwards (16F, Ca-HCO₃ type) sample.

Chemical water type	pH	T (°C)	Ca (mmol/L)	HCO ₃ (mmol/L)	Mg (mmol/L)	Na (mmol/L)	log ^P _{CO₂} (atm)	SI calcite	SI dolomite
Ca-HCO ₃ (16F)	6.72	22.1	1.71	6.1	0.94	0.65	− 1.28	− 0.35	− 1.02
Na-HCO ₃ (35F)	7.54	19.8	0.513	13.2	0.4	15.87	− 1.78	0.01	− 0.01
Balance 35F-16F			− 1.2	7.08	− 0.54	15.22			

consequence of the reduction induced by the organic matter oxidation, and the precipitation of metallic sulfide (Reaction (6)). Besides calcite and dolomite dissolution, SO₄ reduction also contributes to the alkalinity of the system. In this system, cation exchange involves the Ca and Mg uptake and K releases from the exchange complex KX (Reactions (7) and (8)).

As regards to the differences in the composition of the observations and the theoretical case, the changes in the total HCO₃ concentrations in both cases are practically compensated by the calcite and dolomite dissolutions, and by organic matter oxidation (− 1.74 mmol/L). However, the TM is even more oversaturated in calcite and dolomite than the observations. Thus, these last one were also compared with the TMWR case, a theoretical mix with restrictions which predicts a dissolution of 14.2 mmol/L of calcite, a precipitation of 8.6 and 5.3 mmol/L of dolomite and gypsum, respectively, and dissolution of 3.67 mmol/L of CO₂. Despite the feasibility in the occurrence of these reactions, TM shown better results than the TMWR case in comparison with the observations for the case of SO₄ and HCO₃, but both ones over-predicted the Ca and Mg contents.

5. Discussion

The results of the study show that regional groundwater chemical composition in the two aquifers of the MRAS is mostly the result of a few main hydrogeochemical and physic processes. The ionic contents and the stable isotopes values of the less mineralized groundwater samples from the Upper Aquifer show that evapoconcentration is a common process in the whole aquifer system, as has been described for many other water-table aquifers in temperate and semi-arid areas of the world (Craig and Gordon, 1965; Dansgaard, 1964; Salati et al., 1979; Leguy et al., 1983; Gedzelman et al., 1989; Rindsberger et al., 1990; Gat, 1995; Zongjie et al., 2015 among others). Examples of the notable effect of evapotranspiration on shallow groundwater composition near the study area have been reported by Logan et al. (1999) and Zabala et al. (2015).

The dissolution of edaphic CO₂ is a common situation in any water-table aquifer with vegetated soil, as is the case of the Upper Aquifer in the MRAS. Is a well-known situation that dissolved CO₂ in pore water of the unsaturated and saturated zones induces the dissolution of many mineral, and especially of carbonate minerals (Appelo and Postma, 2005). In the Upper Aquifer there is a huge carbonate source in the abundant carbonate crust layers of the Pampeano sediments. Calcite and dolomite dissolution seem to be a fast process, because most of the groundwater samples, even the shallowest, are in or close to equilibrium with both minerals. Thus, most of the groundwater in both aquifers do not have conditions to dissolve or precipitate calcite or dolomite, but obviously this process has to occur when rain water

infiltrates. On the other hand, evapotranspiration concentrates soil water and induces carbonate saturation and precipitation. This mean that both carbonate dissolution and precipitation take place mostly during the transit through the unsaturated zone, and they probably dominate in different climate conditions. A few samples in both aquifers are oversaturated in dolomite. Those samples are moderately saline (EC around 1 mS/cm), and the cause –that remains unknown– must be local. Many works carried out in the Pampeano and Postpampeano sediments, which form the Upper Aquifer in this work, claim the occurrence of both carbonate dissolution and precipitation in those formations (Fidalgo et al., 1975; Panarello et al., 1995; Auge, 2004; Taboada, 2006; Zabala et al., 2014, 2015).

Most of the samples studied in both aquifers are subsaturated in gypsum, so if this mineral were present in the sediments, it would dissolve. Logan and Nicholson (1998) and Logan et al. (1999) found gypsum in the same geological formations studied in the MRB but in La Plata coastal plain, to the east of the MRB. Potential SO₄ sources were spatially discriminated in the MRAS. For the Upper Aquifer a main potential source is pollution, mostly from liquid and solid domestic wastes. But this is a less probable source of sulfate for the confined Puelche Aquifer. In both aquifers, SO₄ in groundwater of the lower part of the basin is associated mostly to mixing with marine water, as notice the high concentration values of boreholes 32F, 32P, 27F and 27P. However, Logan and Nicholson (1998) found that the SO₄ contents at La Plata derived from three sources: mixing with encroached sea water, pyrite oxidation (with later SO₄ reduction) and gypsum dissolution. In the MRAS, SO₄ excesses observed in the middle and upper parts of the Puelche Aquifer could also derive from sulfide oxidation and/or from gypsum dissolution. Both minerals could be hosted into the clayey top layers of the Puelche Aquifer, as points out the SO₄/Cl ratio (in meq/L) differences between top and bottom samples within the aquifer. Sulfide minerals could become in contact with atmospheric oxygen as a consequence of piezometric levels drawdown due to intense exploitation of the Puelche Aquifer. However, the presence of sulfide minerals (e.g. pyrite, FeS₂) in those sediments must be confirmed.

With respect to the possible existence of gypsum, Logan and Nicholson (1998) and Logan et al. (1999) claim that gypsum formed in La Plata area during sea water intrusion as a result of gypsum oversaturation in mixed groundwaters. Pyrite oxidation during hot and dry periods, likely soon after the last Quaternary marine transgression (7000–3000 yr BP), also provided sulfate for gypsum formation. The iron from the pyrite remained in the upper and middle layers of the Postpampeano Sediments as FeOOH. Ca came from carbonate dissolution. Though up to now there are not mineral data for the MRAS, the sediments of the Puelche and Upper aquifers have the same sedimentary origin than in La Plata, and they have also been intruded by sea water along the Quaternary. Thus, the processes identified in La Plata area are prone to occur also in the MRAS. But the extent to which this model can be generalized to other coastal regions of Argentina and Latin America will depend on further investigation.

Silicate dissolution, mostly of albite, anorthite and K-feldspar, are also probable reactions occurring in the MRAS. The work performed shows that albite and K-feldspar dissolution would take place mostly in the unsaturated zone and in the shallowest saturated zone. Anorthite dissolution could occur at greater depths. However, in the MRAS the dissolution of the three minerals does not contribute significantly to the

Table 2

Reaction quantities from model 1a_inv and 1b_inv. Positive values indicate mineral dissolution whereas negative ones indicate precipitation.

	Calmite (mmol/L)	Dolomite (mmol/L)	Na (mmol/L)	Ca (mmol/L)	Mg (mmol/L)	CO ₂ (mmol/L)
M1a_inv	− 0.66	3.26	15.22	− 3.8	− 3.8	1.22
M1b_inv	5.87	−	15.22	− 7.07	− 0.54	1.21

Table 3

Measured (Original 35F) and modeled composition of sample 35F using model 1a_dir and model 1b_dir. See main text for complementary information.

	pH	Ca (mmol/L)	HCO ₃ (mmol/L)	Mg (mmol/L)	Na (mmol/L)	logP _{CO2} (atm)	SI calcite	SI dolomite
Original 35F	7.54	51.3	13.2	39.9	15.9	-1.7	0.1	-0.01
35F M1a_dir	7.5	41.6	11.5	0.08	10.3	-1.7	0.1	-0.58
35F M1b_dir	7.54	36.6	12.5	40	10.8	-1.7	0.1	-

groundwater chemical composition. Other authors also claim the existence of silicate dissolution in other zones of the geological formations studied here (Londoño et al., 2008; Martínez et al., 1998; Martínez and Osterrieth, 1999), but only Zabala et al. (2014) mention the scarce contribution of this process to groundwater chemistry.

Cation exchange with Na release and mainly Ca uptake is one of the major hydrogeochemical processes at regional scale, and induces the main chemical evolution observed in groundwater, from Ca-HCO₃ or MgCa-HCO₃ water types to a Na-HCO₃ type. This evolution is rather fast and is observed only in lowly mineralized samples of the Upper Aquifer. All the lowly mineralized samples of the Puelche Aquifer are of the Na-HCO₃ type and have the same cationic contents and Na/Cl (molar) ratios than those of the Upper Aquifer. This means that cation exchange takes place mostly during and shortly after recharge, and that during groundwater transfer to the deeper aquifer there is not additional exchange. Cation exchange is a major process leading the occurrence of Na-HCO₃ groundwater in many aquifers around the world (Appelo, 1994; Toran and Saunders, 1999; Carol et al., 2012), and it is known to occur in the Pampeano Sediments (part of our Upper Aquifer) across NE Argentina (Logan and Nicholson, 1998; Auge, 2004; Auge et al., 2002; Londoño et al., 2008; Zabala et al., 2014). However, this is the first work identifying that cation exchange takes place just in the initial stages of the groundwater flow network.

On the other hand, although cation exchange processes in the overall basin involve the Na release and Ca uptake, the cationic composition of the samples 37P (which is practically sea water); 29P (a marine-type saline water) and 26F (a Ca-Cl-HCO₃ type water) are explained by Ca (and may be Mg) release and Na uptake. This is assumed to be the result of an active salinization process in the lower basin zone, where boreholes 26F, 29P and 37P are located.

The fact that both aquifers share the main chemical facies (Na-HCO₃) and mineralization degree suggests a relevant hydraulic connectivity between them, which is also supported by the hydrodynamic studies carried out (IHLLA, 2012; Ceballos et al., 2016).

6. Conclusions

The study has identified the leading hydrogeochemical processes responsible for the regional groundwater chemistry of the two aquifers of the Matanza Riachuelo Aquifer System.

In the unconfined Upper Aquifer, the water type most widely found is fresh (EC from 0.6 to 1.5 mS/cm) Na-HCO₃ water. It is the result of a few main hydrogeochemical processes: edaphic CO₂ dissolution, calcite and dolomite dissolution, and cation exchange, and of one physical process, evapotranspirative concentration. These processes occur in the shallowest part of the aquifer, during or shortly after groundwater recharge. From a quantitative point of view, cation exchange is the most significant process controlling the cationic contents. In the same aquifer, saline waters (EC from 6 to 10 mS/cm) of the Na-Cl type are found in the lower basin (NE part). They are the result of fresh, Na-HCO₃ water type mixing with marine groundwater encroached or connate in the sediments of the aquifer's geological formations (Postpampeano and/or Pampeano sediments).

The most frequent water type in the deep, semiconfined to confined Puelche Aquifer shows similar features than the Na-HCO₃ waters in the Upper Aquifer, though the less mineralized samples of the Puelche are slightly more mineralized (CE ≈ 0.8 mS/cm) than those of the Upper Aquifer. This reflects the fact that the main source of water for the Puelche Aquifer is the Upper Aquifer. At regional scale, there are not major hydrogeochemical processes inducing chemical changes in the Puelche Aquifer. At local scale, in the upper and middle reaches of the basin sulfate contents increase significantly, more notably in the top of the aquifer. Three potential sources or sulfate were evaluated: (1) agriculture and/or sewage; (2) sulfide minerals, hosted in the overlying units of the Puelche Aquifer; (3) gypsum, which would also be present in the overlying sediments to the Puelche Aquifer. The study performed suggests that pollution is quantitatively irrelevant, and that dissolution of sulfide minerals is less probable, in hydrodynamic terms, than dissolution of gypsum. It also suggests that even being a widespread process, the solution of sulfur from its mineral sources takes place on a local basis. However, additional specific research should be conducted to identify the real source/s of SO₄.

Finally, both in the lower and in the upper parts of the basin, groundwater salinity in the Puelche Aquifer increases and the main chemical facies evolves to NaCa-SO₄Cl and Na-Cl. This is the result of mixing between Na-HCO₃ waters and marine water from different origins: connate marine water from the underlying Paraná Formation in the upper basin (the only source of marine-like salinity in this zone), and encroached seawater from Pleistocene and Holocene marine transgressions into the Puelches Formation in the lower basin. Nevertheless, the

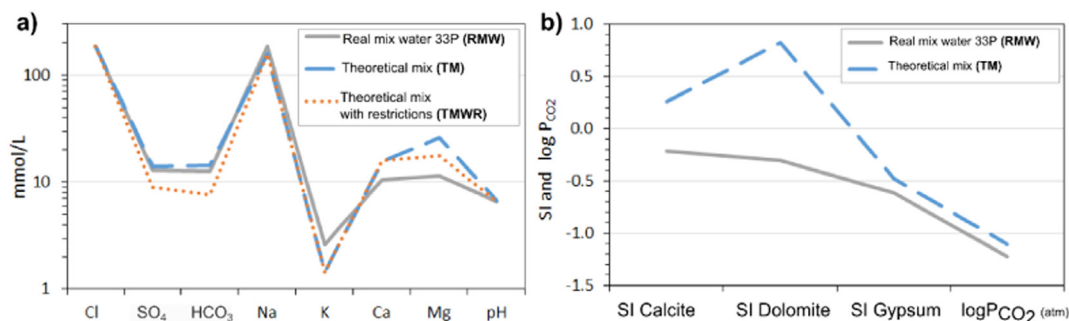


Fig. 11. a) Solute concentrations (mmol/L) of the real mixed sample 33P (RMW), theoretical composition of the same sample modeled without thermodynamic constraints (TM), and theoretical composition modeled with thermodynamic restrictions (TMWR). b) Saturation indices and CO₂ content (log P_{CO2}, atm) of waters RMW and TM.

saltier groundwater sample belongs to borehole 37P (50.37 mS/cm) in the lower basin, whose Cl content ($Cl = 19,210 \text{ mg/L}$) is similar to standard sea water. This borehole is screened at the bottom of the Puelches Formation, close to the clayey sediments of the Paraná Formation, so this formation could be also a source of salinity in the lower basin.

In summary, at basin scale the main processes guiding the chemical composition of groundwater in the two aquifers are cation exchange and mixing of fresh groundwater with sea water of diverse origins and ages in different zones of the basin. The first process is hydrogeochemical; the second is purely physic, but influences groundwater composition dramatically. Both processes are controlled by different kind of factors, but mixing, which is the one potentially inducing stronger quality limitations, can be addressed through an adequate aquifer management scheme provided the existence of sound scientific knowledge about the zones where they occur, the origin of sea water, and the actual and past hydrodynamic conditions.

On a general dimension, the work highlights the relevance of performing detailed studies on groundwater chemistry and its origin to understand the main factors controlling groundwater chemistry and quality both at regional and local scales. This knowledge is needed to design effective management programs, and it must be generated even if it is not used in the short term. Locally, the results of this investigation provide the conceptual framework supporting different numerical modeling approaches under development in the MRAS, which address diverse quality and quantity aspects.

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