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Groundwater chemical baseline values to assess the Recovery Plan in the Matanza-Riachuelo River basin, Argentina

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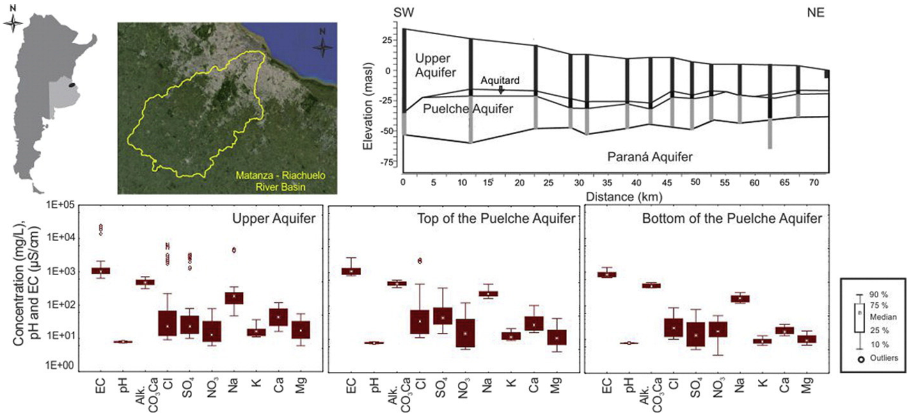
HIGHLIGHTS

- Groundwater chemical baseline has been studied in the Matanza-Riachuelo basin.
- Concentration ranges and statistical values at three depths are established.
- The main sources and processes behind groundwater chemistry are identified.
- Upper baseline limits are proposed to support operating remediation actions.
- The methodology used is the proposal to support European water directives.

GRAPHICAL ABSTRACT



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ABSTRACT

The two most exploited aquifers in the Matanza-Riachuelo River basin are being monitored in the framework of the Integrated Environmental Sanitation Plan that implements the Basin Authority, Autoridad de Cuenca Matanza Riachuelo. In this context, this work identifies the groundwater chemical types and the natural processes behind them; determines spatial and temporal changes; establishes ranges of variation for chemical components, and proposes concentration values for the upper limit of the natural chemical background. A total of 1007 samples from three aquifer-layers (Upper Aquifer, top and bottom of Puelche Aquifer) have been studied. As concrete guidelines for practical determination of baseline values are not available in the region, the methodology used follows the proposals of European projects which assessed European water directives.

The groundwater composition is very stable in terms of both chemical facies and mineralization degree, and the changes observed in the dry and wet periods analysed are subtle in general. Most of the groundwater is Na-HCO_3 type, except a few samples that are Ca-HCO_3, Na-$ClSO_4$ and Na-Cl types. The Ca-HCO_3 waters are the result of calcium carbonate dissolution, Na-HCO_3 waters result from cation exchange and carbonate dissolution, while in the Na-$ClSO_4$ and Na-Cl waters, mixing with connate and with encroached old marine water from the underlying and overlying sediments are the most relevant processes. The proposed values for the upper limit of the natural

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background consider the influence of geology and Holocene marine ingressions in the baseline of coastal groundwater.

This study allowed to know the initial chemical conditions of the groundwater system of the Matanza-Riachuelo River basin and to establish the reference from which Basin Authority can start to evaluate trends and monitor the recovery plan. At the same time, it sets a precedent for future studies in the region.

1. Introduction

All over the world, groundwater is an important resource for drinking water supply, irrigation, industrial development, and ecosystems and stream flow maintenance. Increasing demand and trends towards climate change are placing pressure on groundwater resources, and it is crucial to notice that, for some main uses, the available quantities are restricted mostly by quality aspects. The chemical composition of groundwater, and its derived quality, are influenced by a variety of actors related to both natural and anthropogenic causes, such as recharge water composition and rate, aquifer mineralogy and the relative reactivity of the minerals, groundwater residence times, groundwater exploitation pattern, or the existence of agricultural, industrial and/or urban activity affecting groundwater quality (Custodio and Llamas, 1996; Domenico and Schwartz, 1998; Appelo and Postma, 2005). However, in the absence of pollution, groundwater chemistry mainly reflects the mineralogical composition of the terrain, and their variability and degree of mineralization depend mainly on the residence time in the aquifer. This natural composition, also called chemical background and chemical baseline, provides groundwater its natural quality. The natural background levels are a range of values, rather than a single value (Edmunds et al., 2003; Edmunds and Shand, 2008).

The current worldwide awareness for groundwater quality protection has taken the baseline quality subject to the regulation scenario. Over the last fifteen years, several countries have advanced in laws and actions to establish the baseline quality of groundwater as an essential prerequisite for groundwater remediation programs and for imposing regulatory limits (Shand et al., 2007; Custodio and Manzano, 2008). For example, in the United States of North America, the Environmental Protection Agency and the United States Geological Survey have been applying the term *baseline* to natural groundwater quality since the decade of the 1990s. In Australia, the recently updated Guidelines for Groundwater Protection (GGP, 2013; first adopted in 1995 within the National Water Quality Management Strategy) state that guidelines for groundwater protection rely on a framework that requires the identification of existing and potential "environmental value" categories for groundwater, and that "environmental categories" should be determined through baseline assessment of groundwater quality. In the European Union, the Water Framework Directive (EC, 2000) establishes the setting to protect water resources in order to improve current status and prevent any further environmental deterioration, and the Groundwater Directive (EC, 2006) establish strategies to prevent, control and correct groundwater contamination on the basis of natural background levels and threshold values (Wendland et al., 2007). In this context, two European research projects, BASELINE (2003) and BRIDGE (2009) were promoted to establish concepts and definitions and to standardize criteria and methodologies for the determination of groundwater background levels and threshold values.

In Argentina, Articles 41 and 43 of the National Constitution laid the basic principles to guarantee the right to a healthy and balanced environment, the obligation to restore the environment, and the right to pursue legal action in order to protect the environment. From this basis, and taking into account that in Argentina the management of resources is decentralized and whereby each jurisdiction have the original dominion over the natural resources (including surface and groundwater) within their territory, the Nation promulgates rules to ensure environmental protection, and the other jurisdictions promote the necessary laws to reinforce the former ones. The national policy guiding water resources management is embodied in the Environmental General Law (Ley 25.675, 2002) and in the Regime of Environmental Management of Water (Ley 25.688, 2002). These two laws establish the objectives and principles of environmental policy, as well as rules for the use and preservation of water. To this respect, the National Authority has the responsibility to determine the maximum acceptable limits for water pollution according to different uses, to define guidelines for aquifer recharge and protection, and to set up the parameters and environmental standards of water quality. This latter, although not establishes an explicit requirement to define the baseline water quality, provides a basis to do it. The present work is concerned to this matter.

The Matanza-Riachuelo River basin (MRB) covers part of the Autonomous City of Buenos Aires (Ciudad Autónoma de Buenos Aires, CABA) which occupies the NE part of the basin, and 14 other municipalities. The Matanza River flows from SW to NE and discharges into the Río de la Plata. The lowest section of the river is called Riachuelo. The MRB it is the most populated (more than 4 million people, which is 10 % of Argentina's population), industrialized and polluted basin in Argentina. Since the beginning of the 19th Century the basin experienced a steady degradation of water, soil and air quality, mainly in the Riachuelo section. The lower river course was broaden and channeled, and the recurrently flooded lowlands of former meanders were occupied by salted-meat factories, and by densely populated unplanned villages of the low-income population. Along two centuries, the same area has been taking in different but intensely polluting industries like petroleum refineries and petrochemical facilities.

Groundwater has been extensively used across the MRB, especially since the second half of the XX century. In the 1990s, the abstraction boreholes used to supply the lower basin were gradually abandoned due to high nitrate contents, and they were partly replaced with imported water from the Río de la Plata. However, in the middle and upper parts of the basin groundwater remains the main source of supply for domestic, industrial and agricultural uses.

Due to the chronicle environmental degradation, 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 MRB (CSJN, 2008). Complying with this requirement, ACUMAR designed and implemented the Integrated Environmental Sanitation Plan (Plan Integral de Saneamiento Ambiental, PISA), and from 2008 begun monitoring activities of groundwater, surface water, sediments and air. The PISA does not content explicit requirements to determine the natural baseline quality of the groundwater, and this neither arises from the legal requirements that the Justice Court imposed to ACUMAR. However, knowing and understanding both the influenced present-day groundwater quality conditions and the baseline ones can be a very useful tool to assess monitoring and trends evaluation within the recovery plan.

The main objective of this work is to understand the groundwater baseline chemistry in the two more used aquifers underlying the MRB, the Upper Aquifer, which is a water table one, and the semiconfined Puelche Aquifer. The concrete objectives are: to identify the groundwater chemical types and the natural processes producing them; to know possible spatial and temporal chemical changes in relationship with seasonal hydrological changes; to establish ranges of variation for major, minor and some trace components, and to propose concentration values for the upper limit of the natural background ranges as references for the remediation actions. The study is part of the activities conducted in the framework of the *Groundwater Project in the Matanza-Riachuelo Basin*, which is being developed by ACUMAR and the “Dr. Eduardo J. Usunoff” Large Plains Hydrology Institute (Instituto de Hidrología de Llanuras Dr. Eduardo Usunoff, IHLLA, Argentina). The project aims at providing studies and tools to establish guidelines and to assess the application of the PISA to the recovery of groundwater quantity and quality.

2. Study area

2.1. General features

The MRB is located to the E of Argentina and the NE of Buenos Aires Province (Fig. 1). It includes part of the CABA and the municipalities of Lanús, Avellaneda, Lomas de Zamora, Esteban Echeverría, La Matanza, 'Ezeiza, Cañuelas, Almirante Brown, Morón, Merlo, Marcos Paz, Presidente Perón, San Vicente, and General Las Heras.

With a surface of 2065 km^2 and a typical “pampa” (plain) landscape, the catchment spreads between the Salado River basin to the SW, and the Río de la Plata to the NE. The main course is the Matanza River, which flows NE along 70 km before to be renamed Riachuelo some 15 km before pouring into the Río de la Plata.

The area has a temperate climate with warm summers, cool winters and prevailing winds from the E and NE. Annual precipitation increases notably from SE to NW: average rainfall recorded at the Buenos Aires city station of the National Meteorological Survey of Argentina (SMN in Fig. 1) for the period 1956–2008 was 1193 mm/year, while at the Ezeiza station (in the middle of the basin, see Fig. 1) it was 1008 mm/year. Monthly precipitation shows a clear seasonal pattern, with lower values in the cold season (May to September) and higher in the warm season (October to April). Potential evapotranspiration in Buenos Aires station (after Penman-Monteith) is 1277 mm/year, which means that the soil has water deficit (Vives et al., 2012).

The whole CABA, together with the fourteen municipalities integrating the MRB, concentrate more than 8,213,000 inhabitants, of which about 4,363,000 settle within the hydrographic basin. The MRB hosts 7200 industries mainly of the metallurgical, food, textile, footwear and chemical sectors. Based in ACUMAR data, the lower basin concentrates 70 % of the population and 63 % of the industries, while in the middle basin peri-urban and consolidated urban areas coexists with 33 % of the total industries. In contrast, the upper basin is predominantly rural, with about 400 industrial and agricultural–livestock establishments, and acceptable environmental conditions persist here.

Estimates of water supply and sanitation services coverage for year 2010 indicate that 85 % of the people had drinking water supply and 75 % were connected to main sewerage (PISA, 2010). These services have been progressively increasing with the implementation of the PISA. The areas yet without service locate in the middle and upper sectors of the basin, where the residents have their own on-site solutions through septic tanks or pits and private supply boreholes.

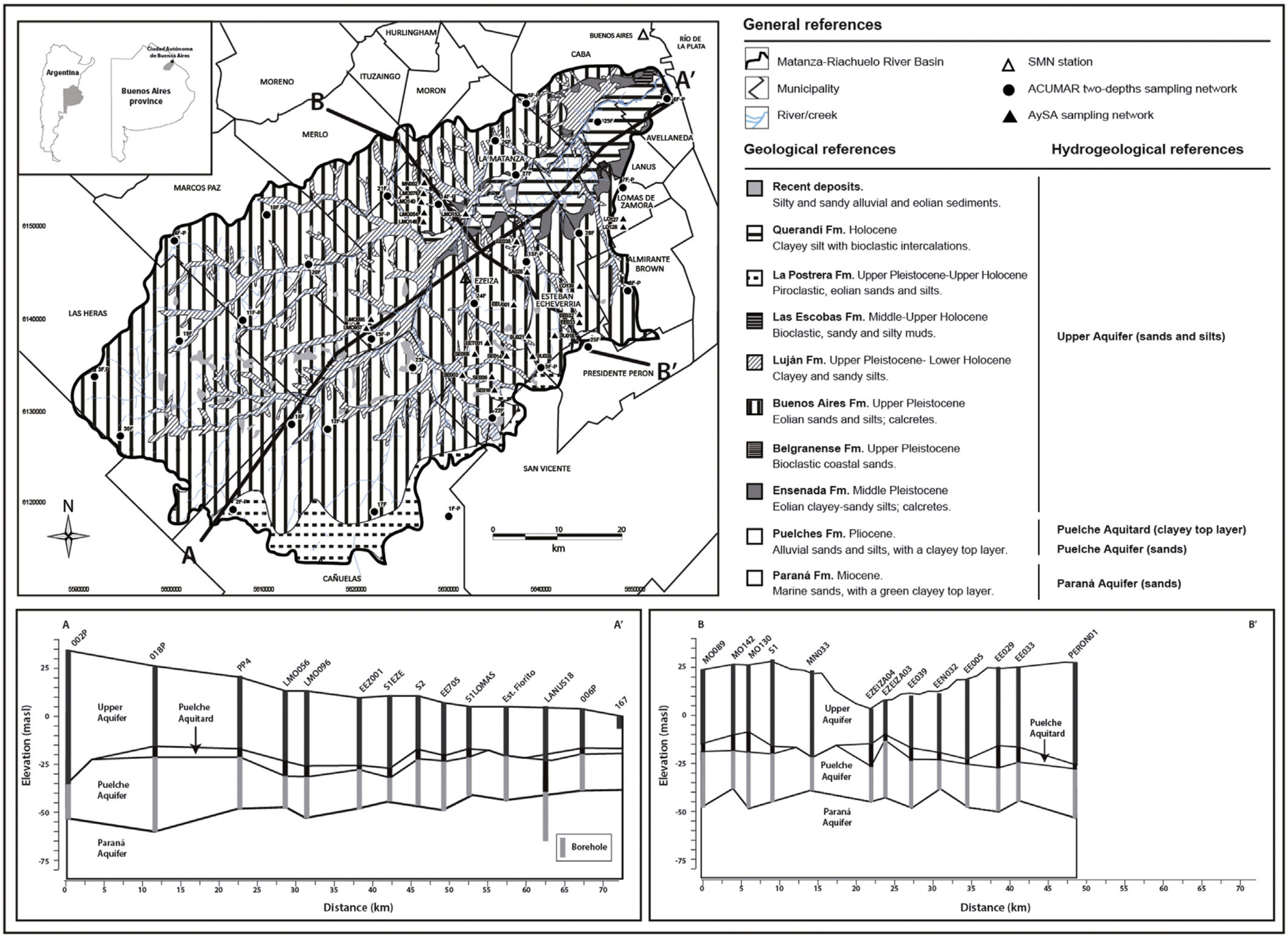

Fig. 1. Location of the Matanza-Riachuelo River basin and illustrative hydrogeological cross sections. Sampled boreholes and wells used for the study are also shown.

2.2. Geology and mineralogy

The MRB is a sedimentary basin filled up by continental and marine sediments deposited over a crystalline Precambrian basement. This one is formed by gneisses, migmatites, amphibolites and granitic plutons (Dalla Salda et al., 2006), and crops out in the Tandilia Range, some 250 km to the SW of the MRB, and also in the Río de la Plata, some 50 km the N of the MRB. The top of the basement deepens to the SW, which causes the sedimentary formations overlying it to thicken in the same direction. In the lower MRB basin the top is at 265 m depth and in the middle basin it is at 370 m depth. There is not information about the upper basin.

Overlapping the basement there is the Olivos Formation (Oligocene-Miocene), a continental formation of aeolian and fluvial origin formed by sands (lower part) and clays (upper part) with gypsum (Auge, 1986, 2004). Within the MRB the thickness ranges from.

195 to 256 m. The Olivos Formation is covered by the marine Paraná Formation, which formed during a broad transgression in middle to lower Upper Miocene. It is sandy to the bottom and clayey to the top, and has randomly distributed carbonated layers (Aceñolaza, 2000). It holds original marine (saline) and diluted (brackish) pore water in many areas. In the study area, the top of the Paraná Formation is at 40 m depth in the NE and at 89 m depth in the SW (Mancino et al., 2013), and its thickness varies between 13 and 323 m. The mineralogy of the Paraná Formation is mostly siliceous.

Over the Paraná Formation there is the Puelches Formation (Early Pliocene), mostly fluvial but with some aeolian components (Logan et al., 1999). Within the MRB the thickness ranges between 13 and 33 m. It is formed by yellowish uncemented quartz sands, with local thin intercalations of gravels and clays (Santa Cruz, 1972). Clay abundance increases toward the top, where there is a set of thin silty and clayey layers with a variable joint thickness between a few decimeters and almost 40 m, and a heterogeneous spatial distribution, though they tend to thicken to the SW. This clayey layers appear at 14–15 m depth to the NE of the MRB, and at 63–77 m depth to the SW (Mancino et al., 2013). The Puelches Formation is composed mostly by quartz (87–93 %), and to a lesser extent (3–6 %) by feldspars (orthoclase and microcline) and plagioclase (oligoclase and andesine). There is also a minor presence of lithoclasts, alterites, glass, calcite, pistacite, zoisite, clinozoisite, tourmaline, garnet, staurolite, kyanite, rutile, and amphibole (hornblende) (Santa Cruz, 1972).

On top of the Puelches Formation there are the Pampeano Sediments (Pleistocene-Holocene) (Fidalgo et al., 1975), mostly of eolian origin but with fluvial and lacustrine deposits. The aeolian fraction consists of sandy silts and loess with a volcanic (Andean) origin (González Bonorino, 1965; Tófalo et al., 2005). These sediments cover an extended area in NE Argentina, forming the large plain area called Pampa. In the study area the Pampeano Sediments are composed of two geological formations, the Ensenada Formation and the Buenos Aires Formation (Riggi et al., 1986). Both formations consist of clayey to sandy silts and loess of fluvial, lacustrine, and eolian environments, with nodular and stratiform $CaCO_3$ at shallow depths (Frenguelli, 1955; Fidalgo et al., 1975).

Partially overlying the Pampeano Sediments are the Postpampeano Sediments (Holocene) (Fidalgo et al., 1991), which are composed of several geological formations. The Luján Formation (Late Pleistocene-Lower Holocene) (Fidalgo et al., 1973, 1975), of fluvial origin, consists of clayey and sandy silts rich in carbonate, chloride and sulfate minerals of channel and floodplain facies (EASNE, 1973). In some valleys, partially covering the Luján Formation appears La Plata Formation (Middle to Upper Holocene) (Frenguelli, 1957), which consists of bioclastic sandy and silty mud of fluvial, lacustrine and marsh environments. La Postrera Formation (Late Pleistocene- Late Holocene) (Fidalgo et al., 1973, 1975) was deposited under arid conditions, and is composed by materials deflated from the alluvial environments and re-deposited as sandy eolian sediments. The Querandinense (Logan et al., 1999) or Querandí (Frenguelli, 1957) Formation was formed during the Holocene. Sea level fluctuations caused several transgressive and regressive episodes in the zone (Amato and Silva Busso, 2006), causing the inundation and retreat of the coastal plain and the lower tract of the alluvial valleys several times, and the formation of tidal plain, coastal lagoon and marsh deposits. Those sediments are mostly clayey silts with bioclastic intercalations, and they hold saline pore water (Logan et al., 1999). Finally, partially covering all the Postpampeano formations there are recent sandy and silty alluvial sediments, sandy eolian deposits, and sandy, silty and clayey deposits of deltaic origin.

The mineralogy of the Pampeano Sediments consists of plagioclase, quartz, K-feldspar, volcanic glass, calcite, opal, micas, and some heavy minerals (magnetite, titanite, ilmenite). Pyroxene and amphibole are the less abundant minerals, while montmorillonite and illite dominate in the clay size fraction (Teruggi, 1957; González Bonorino, 1965; Martínez et al., 1998; Tófalo et al., 2005; Bonorino et al., 2008).

The joint thickness of the Pampeano and Postpampeano sediments decreases from SW to NE within the MRB, with a maximum joint thickness of 70 m in the SW, and a minimum of about 13 m in the NE (Mancino et al., 2013).

2.3. Hydrogeology

The main hydrogeological characteristics of the geological formations underlying the MRB are as follows:

- The lower sandy layers of the Olivos Formation behave as a confined aquifer of medium to low productivity (Auge, 1986, 2004), while the upper clayey layers behave as an aquitard. The presence of gypsum and anhydrite contributes to high concentrations of sulphate and elevated salinity (6–60 g/L) (Auge et al., 2002).
- In the *Paraná* Formation, the lower sandy section behaves as a confined aquifer, while the upper clayey section behaves as an aquitard. Likewise to the Olivos Formation, the exploitation of the *Paraná* Formation is constrained by its high salinity. Auge (1986, 2004) reported values of 3–4 g/L of total salinity within the MRB.
- The lower sandy section of the Puelches Formation also behaves as a confined aquifer of medium to high productivity, while the top clayey layers behave as an aquitard (Auge, 1986, 2004). This formation holds the main and most exploited aquifer in the MRB, which is called Puelche Aquifer. It holds good quality water in most of the basin (more information is provided below). The aquitard has a discontinuous distribution. In many sectors of the lower and middle basins this aquitard does not exist in practice, and the Postpampeano and Pampeano sediments are in direct contact with the sand layers of the Puelches Formation, but to the SW of the MRB it has been found in all the recently drilled monitoring boreholes.
- The Pampeano and Postpampeano sandy and silty sediments behave as a sole aquifer, which is called Upper Aquifer in this work. This aquifer holds the water table, and its upper part behaves as unconfined while the layers below some 25–30 m depth behave as semi-confined. It has medium to low productivity and a variable water quality (more information is provided below).

Under natural flow conditions recharge to the Upper Aquifer occurred mostly by infiltration of meteoric water. Nowadays, in the most populated areas there are other recharge sources, as losses of water networks, sanitation and storm drains, and leaching from septic tanks. This has clear consequences to groundwater quality. Also under natural conditions, discharge occurred to streams, rivers, lagoons, Río de la Plata and through evapotranspiration (EASNE, 1973; Vives et al., 2013). Under the present day influenced conditions, groundwater withdrawals and vertical transfer to the underlying Puelche Aquifer seem to account for a notable discharge proportion, which is still under evaluation (Vives et al., 2013).

The Puelche Aquifer does not crop out within the MRB. It is recharged mostly by vertical transfer from the Upper Aquifer (Auge, 1986; Vives et al., 2013), especially in the upper and middle parts of the basin. The northern, coastal area of the Puelche Aquifer contains encroached seawater from the last Quaternary sea level rises.

The two aquifers show similar piezometric patterns in almost the whole basin, and in both of them regional groundwater flow goes from SW to NE (UNLP, 2010). The water table surface reflects clearly a strong relationship with the streams, especially with the Matanza-Riachuelo River. Vertical hydraulic gradients have been observed in different zones of the basin: downward gradients dominate to the W, N and SE, while to the middle and lower sectors of the basin upward gradients are common (Melián, 2014). In the upper and middle parts of the basin, the piezometric levels of the Upper Aquifer and those of the upper part of the Puelche Aquifer respond simultaneously to seasonal recharge elevations and dry-season drawdowns, showing a strong connection of both aquifers at regional scale. A similar behavior is observed in some areas of the middle and lower sectors of the basin, though here the oscillations are associated with the management of the aquifers. This is consistent with the geological observations, and confirms that the aquitard at the top of the Puelche Aquifer is not continuous (Vives et al., 2012, 2013; Melián, 2014). In fact, many previous works state that the two aquifers form a unique multi-layer system (EASNE, 1973; Santa Cruz and Silva Busso, 2002; Auge, 2004; UNLP, 2010).

There are a number of previous works dealing with the hydrochemistry of the Pampeano and the Puelches formations in the MRB, though few of them consider the whole basin. EASNE (1973) and UNLP (2010) performed regional studies, but most of the existing reports are local and focus mostly in the middle and lower sectors of the basin (Santa Cruz et al., 1997; Santa Cruz and Silva Busso, 2002; Carol, 2003; Auge, 2004; Amato and Silva Busso, 2006; HIDROAR, 2009). All the studies show that both aquifers have quite similar fresh groundwater in the southern and central areas, and in both of them groundwater salinity increases from SW to NE. Fresh groundwater in the Upper Aquifer (commonly called Pampeano Aquifer in those works) is of the Ca-HCO_3 type when recently recharged, and it changes to Na-HCO_3 along flow due to cation exchange processes. Fresh groundwater of the Puelche Aquifer is also of the Na-HCO_3 type, reflecting its origin (recharge from the Upper Aquifer) and also the similar mineralogy of the Pampeano and the Puelches formations. In all the works the increase of groundwater salinity to the NE is attributed to several factors, including mixing with marine porewater (in the Postpampeano Sediments and in the Puelches Formation), evapo-concentration, and the possible upwards discharge of deeper aquifers (Paraná Formation). Several studies carried out in basins close to the MRB and sharing the same aquifers show the same main groundwater chemical types and point to the same physical and hydrogeochemical processes to explain them (Logan and Nicholson, 1998; Logan et al., 1999; Heredia et al., 2003; Bonorino et al., 2008; Carol et al., 2012; Carretero et al., 2013, among others).

In the framework of the ACUMAR-IHLLA *Groundwater Project in the Matanza-Riachuelo Basin*, a preliminary hydrogeochemical study of the Upper and Puelche aquifers in the whole MRB was performed in 2011 (Manzano and Zabala, 2012; Manzano et al., 2013), and a complete study including hydrogeochemical modelling and mixing calculations of multiple groundwater sources has been performed recently (Manzano et al., 2015). This is the subject of papers under preparation.

3. Materials and methods

To perform this study a total of 1007 groundwater samples have been used, 570 from the Upper Aquifer, 322 from the top of Puelche Aquifer and 115 from the bottom of Puelche Aquifer. Major chemical components (Cl, SO_4, alkalinity — as $CaCO_3$, Na, Ca, Mg, K, NO_3), some minor components (NH_3, NO_2), trace components (H — as pH, As, Cu, Fe, Mn, Total N, and Zn), and Electrical Conductivity (EC at 25 °C) and temperature (T °C) have been used. The trace components studied are those that were reported above their respective detection limits in the ACUMAR analysis. The number of minor and trace components analysis is somewhat smaller than that of major components due to a different sampling frequency.

Samples from the Upper Aquifer and top of Puelche Aquifer were taken in the ACUMAR double-depth monitoring network covering the whole basin, which by the time this work was performed consisted in one borehole screened in the Upper Aquifer (Table 1) and a second borehole screened in the top of the Puelche Aquifer (Table 1). Forty-four boreholes, distributed in 29 locations, were sampled in 24 field surveys between May 2008 and September 2011. Analysis of major, minor and trace components were performed at the University of La Plata (UNLP) for the period 2008–2009 and at the National Institute of Water (Instituto Nacional del Agua, INA) for the period 2010–2011. The samples were taken following the standard procedures for groundwater sampling, which were agreed in a protocol between ACUMAR and INA. Alkalinity, EC and T were measured on site. All the analyses were performed following the methodology proposed by the American Public Health Association (APHA, 2005). All the chemical analyses had ionic balance errors smaller than 20 %, and 67 % of the analysis used had errors smaller than 10 %.

In addition, samples from the bottom of Puelche Aquifer were taken in supply wells of the company Argentinian Water and Sanitation (Agua y Saneamientos Argentinos, AySA). The studied samples belong to 25 boreholes sampled between 2003 and 2010 and located mostly in the NE of the MRB (see Fig. 1). They are 56 to 84 m deep and have screen intervals shorter than 12 m (Table 2). The wells were selected on the basis of their proximity to ACUMAR network locations and the availability of technical characteristics. Physico-chemical parameters, major, and some trace components were analysed in the AySA laboratory. With respect to trace components, most of the AySA analysis reported concentrations under their detection limits (which were set equal to the limits of the Argentina Drinking Water Quality Standards). For this reason, the only component with significant analytical values is As. The analysis used for the study had ionic balance errors smaller than 10%.

As concrete guidelines for practical determination of baseline values are not available in Northern and Southern America, the methodology used follows the proposals of the European Research projects BASELINE and BRIDGE projects (BASELINE, 2003; BRIDGE, 2009). This methodology has been applied to the samples available for the three aquifer-layer studied, Upper Aquifer, top and bottom of Puelche Aquifer. The methods used are as follows:

a) To identify groundwater chemical types and the possible physico-chemical processes producing them, Piper, Schöeller and Stiff diagrams have been used, though in this paper only Stiff diagrams are shown. When this work was carried out the identification of physical and hydrogeochemical processes originating the observed groundwater chemistry was performed just on the basis of the experience of the authors and on other authors' work in the same aquifers but in other basins (Logan and Nicholson, 1998; Martínez et al., 1998; Logan et al., 1999; Miretzky et al., 2001; Bonorino et al., 2008; Quiroz Londoño et al., 2008; Kruse et al., 2010; Carol et al., 2012; Martínez and Osterrieth, 1999, 2013; Zabala et al., 2015). A detailed hydrogeochemical study was not performed then, but it has been performed recently (Manzano et al., 2015).
b) Basic statistical calculations, cumulative frequency curves and box plots have been used to determine concentration ranges. Calculations and graphics have been performed with the software Statistica 8.
c) To identify the possible occurrence of temporal chemical changes related to hydrological seasonality, the composition of boreholes and wells (of the three studied layers) in two periods corresponding to extreme hydrological conditions was compared: a dry period, identified by the lowest water table and piezometric levels recorded,

Table 1
Relevant data of boreholes of the ACUMAR monitoring network.

ACUMAR borehole	Aquifer	Screen interval (m)	ACUMAR borehole	Aquifer	Screen interval (m)
1F	Upper	11.0–14.9	1P	Top of Puelche	58–61
2F	Upper	10.9–13.5	2P	Centre of Puelche	80–83
3F	Upper	10.7–14.5	3P	Top of Puelche	64–67
4F	Upper	10.3–14.3	4P	Top of Puelche	57–60
5F	Upper	3.4–15.5	5P	Top of Puelche	37–40
6F	Upper	2.0–8.3	6P	Top of Puelche	25–28
7F	Upper	5.3–15.9	7P	Top of Puelche	45–48
8F	Upper	2.5–14.4	8P	Top of Puelche	56–59
9F	Upper	10.7–14.1	9P	Top of Puelche	48–51
10F	Upper	10.3–14.0	10P	Top of Puelche	52–55
11F	Upper	10.0–14.3	11P	Top of Puelche	57.5–60.5
12F	Upper	10.2–14.2	12P	Top of Puelche	50–53
13F	Upper	10.2–13.9	13P	Top of Puelche	41.5–44.5
14F	Upper	7.7–16.4	14P	Top of Puelche	34–37
15F	Upper	13.9–17.3	15P	Top of Puelche	33.7–36.7
17F	Upper	5.9–15.2			
18F	Upper	4.1–13.6			
19F	Upper	3.2–13.4			
20F	Upper	9.0–14.1			
21F	Upper	5.0–20.2			
22F	Upper	4.4–14.3			
23F	Upper	5.4–14.3			
24F	Upper	5.8–15.2			
25F	Upper	4.5–15.8			
26F	Upper	Unknown			
27F	Upper	Unknown			
28F	Upper	9.0–20.6			
29F	Upper	4.1–11.6			
30F	Upper	4.3–14.8			

and a humid period, identified by the highest water table and piezometric levels recorded. For the Upper Aquifer and the top of the Puelche Aquifer the driest period was recorded in May–June 2009, and the most humid period in September 2010 (Fig. 2). For the bottom of Puelche Aquifer the samples representative of both driest and most humid conditions were selected from several surveys because some analyses were incomplete. Thus, the driest conditions are represented by samples taken between February 2009 and August 2009, while the most humid conditions are represented by samples taken between November 2009 and March 2010.

Table 2
Relevant data of the AySA exploitation wells.

AySA Well	Depth to top of Puelches Formation (m)	Depth to top of Paraná Formation (m)	Screen interval (m)
LO127	Unknown	Unknown	55–65 (estimated)
LO128	Unknown	Unknown	55–65 (estimated)
LO139	Unknown	Unknown	55–65 (estimated)
LMO957	Unknown	Unknown	47–59 (estimated)
LMO140	Unknown	Unknown	50–60 (estimated)
LMO146	Unknown	Unknown	50–60 (estimated)
LMO153	Unknown	Unknown	50–60 (estimated)
EE032	Unknown	Unknown	59–71
EET001	Unknown	Unknown	55–60/64–69
EEU001	Unknown	Unknown	59–71
EE038	31	54	47–53
LMO054	35	64	52–62
LMO095	40	68	47–59
MN002	40	64	51–63
SA028	38	67	47–53 and 63–66
EE033	49.8	70.1	58–70
SU026	48	74	51–54 and 60–66
SU021	51	80	71–80
SU018	51	81	66–75
SE003	48	67	55–61
SE006	47	73	64–73
SE008	49	78	61–70
SE014	48.7	71.8	55–64
SE016	51	72	60–69
LMO076	37	61	51–60

d) To propose values for the upper limit of natural background ranges for each variable studied the methodology developed in the BRIDGE project has been used. Following Müller et al. (2006), Shand et al. (2007), Wendland et al. (2007), Hinsby et al. (2008), and Coetsiers et al. (2009) the 97.7th percentile of carefully chosen datasets can be used as upper limit when large amounts of data (>60 sampling points) representing groundwater natural composition are available, while the 90th percentile is advisable for smaller datasets or when human impact cannot be excluded from the data. The last aspect should be addressed in the preselection phase, rejecting samples with NO_3 contents >10 mg/L. According to this, samples with ionic balance >10 %, and nitrate contents >10 mg/L have been excluded for this subject. In this work upper limits of natural background were calculated for major chemical components and physical variables using the 90th percentile. Considering the existence of marine sediments with connate water, as well as encroached marine water in continental sediments in the coastal sector of the basin, two values are proposed as upper limits of the natural baseline for the Upper Aquifer and top of the Puelche Aquifer, one value for the coastal area and a second one for the rest of the aquifers.

4. Results

4.1. Groundwater chemical types and possible effects of hydrological seasonality

A detailed study (not shown here) of the chemical time series available for the studied boreholes and wells revealed that the composition of groundwater is very stable in terms of both chemical facies and mineralization degree in almost all the boreholes and wells of the two aquifers, and that the changes observed are subtle in general. In spite of that, the possible occurrence of temporal changes related to hydrological seasonality was checked. The periods chosen and the reason why are described in Section 3. The study is illustrated by means of Stiff diagrams maps (Fig. 3).Stiff diagrams also display the existing groundwater chemical types and their spatial distribution.

Fig. 3 shows the chemical water types in the Upper Aquifer, top and bottom of Puelche Aquifer in a dry, low levels period (figures a, b and c) and in a humid, high levels period (figures d, e and f). The majority of the samples in the three aquifer depths and in the two periods have Na-HCO_3 facies and quite similar mineralization degrees. Thus, groundwater in the Puelche Aquifer has the chemical signature of the Upper Aquifer in most of the MRB area. Moreover, in the major part of the studied locations groundwater chemistry does not experience appreciable seasonal changes (basically, changes in the ratio recharge/evapotranspiration). However, in both aquifers there are some samples with different water types:

- Upper Aquifer: a few samples, dispersed across the basin, are Ca-HCO_3 type (boreholes 1F, 4F, 5F, 8F, 10F and 14F), and two samples in the lower basin are Na-Cl type (6F and 29F). Except borehole 8F, which was not sampled in September 2010, all the other mentioned boreholes showed small chemical changes in the two hydrological periods compared. In the Ca-HCO_3 samples the relative abundances of Ca and Mg changed with recent recharge (humid periods), but their global mineralization did not change. The Na–Cl samples diluted notably in the humid period with respect to the dry one, though they kept their chemical facies: in borehole 29F the EC dropped from 22 mS/cm in July 2009 to 3.6 mS/cm in September 2010, while in borehole 6F it dropped from 7.3 mS/cm to 3.1 mS/cm.
- Top of Puelche Aquifer: two samples in the upper basin are Na-$ClSO_4$ type (boreholes 2P and 12P), and one sample in the lower basin is Na-Cl type (6P). Borehole 2P did not show chemical changes in the two periods compared; changes in borehole 12P cannot be evaluated because it was not sampled in the dry period, but it is likely to behave as borehole 2P. In the coast, borehole 6P had Cl–Na water type in the two periods compared, but its EC decreased from 9.4 mS/cm in the dry season to about 7 mS/cm in the humid one.
- Base of Puelche Aquifer (AySA wells): all the samples are Na-HCO_3 type and they did not show chemical changes between the two compared seasons.

4.2. Ranges of background concentrations

A summary of statistical values for the evaluated physico-chemical variables in samples of the studied aquifers is shown in Table 3. For those components whose contents in groundwater are not influenced –or not significantly- by pollution sources, the range of values between the percentiles 10 and 90 can be considered the natural background levels.

Fig. 4 shows the statistic values calculated for major chemical components and EC values as box plots; Fig. 5 shows the same for minor components (NH_3, NO_2), and trace components reported above their respective detection limits (As, Fe, Mn, Cu, Zn, and total N), and Fig. 6 shows the cumulative concentration curves for major, minor, trace components, and EC values. The main information which can be obtained from those figures and table is as follows:

- The contents of most major components (Cl, SO_4, NO_3, Na, Ca and Mg) range three and four orders of magnitude in the Upper Aquifer and top of Puelche Aquifer, showing large coefficients of dispersion, even larger for the Upper Aquifer. The samples available from the base of the Puelche Aquifer (which represent only the middle and lower zones of the basin where the AySA wells concentrate) show narrower variation ranges, just one or two orders of magnitude, for all major components except NO_3 (Fig. 4). The asymptotic shape of the upper part of the cumulative curves of all the major, minor and trace components in the Upper Aquifer and the top of Puelche Aquifer, and the multi-modal shape of the upper part of many curves in the three studied depths, but especially in the top of Puelche Aquifer, are commented in the discussion section.

- In spite of that, all major components except NO_3 show concentration ranges a little bit larger in the Upper Aquifer than in the top of Puelche Aquifer, and much larger than in the bottom of the last. In fact, with the exception of Na and SO_4, samples from the Upper Aquifer and from top of Puelche Aquifer have quite similar statistical values for the major components, while samples from the base of Puelche Aquifer are more different (Figs. 4 and 6). The range of Na values decreases with increasing depth, though the statistical median is larger in top of the Puelche Aquifer than in the Upper Aquifer and in the base of the Puelche Aquifer (though the last applies just to the zone of the basin where the AySA wells concentrate) (Fig. 4). Sulphate is the only component with the largest range of variation (and median value) at the top of Puelche Aquifer (Fig. 4).
- It was a surprise that most of the samples in the Puelche Aquifer have significant contents of NO_3, with maximum values comparable to those of the Upper Aquifer: 230 mg/L in Upper Aquifer; 270 mg/L at the top of Puelche Aquifer and 119 mg/L at the bottom of the last. However, the median value is smaller at the base of the Puelche (see Figs. 4 and 6).
- The ranges of variation of alkalinity, K and pH values are discrete in all the aquifers, and especially in the Puelche one (top and bottom). The ranges of the three variables decrease with increasing depth (Fig. 4), especially for pH and alkalinity, which have quite small coefficients of dispersion in the base of the Puelche Aquifer.
- The statistic parameters of minor components (NH_3, NO_2) and the trace components reported above their respective detection limits in samples of the ACUMAR monitoring network (As, Fe, Mn, Cu, Zn, and total N) show quite close values in the Upper Aquifer and top of Puelche Aquifer (Fig. 5). Moreover, Cu, Fe, Mn and Zn show comparable variation ranges in the Upper Aquifer and top of the Puelche Aquifer (Fig. 6).
- As is the only component with values reported above the detection limit in the AySA wells. Comparing the three aquifer depths studied, As is clearly more abundant in the available samples of the bottom of Puelche Aquifer (Fig. 6).
- The two trace components of N measured in the ACUMAR monitoring network, NO_2 and NH_3, show comparable dispersion ranges in the Upper Aquifer and top of Puelche Aquifer (Fig. 6).

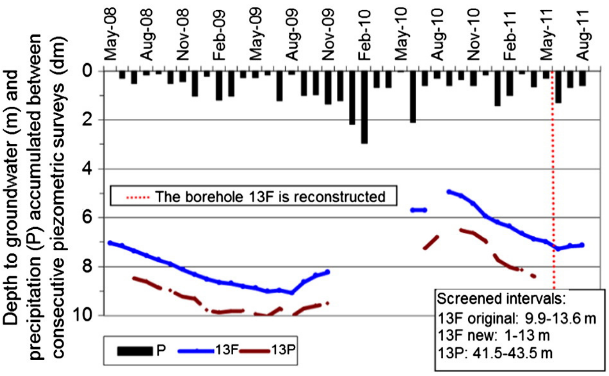

Fig. 2. Groundwater depth evolution in boreholes 13F (Upper Aquifer) and 13P (top of Puelche Aquifer) of the ACUMAR monitoring network. Precipitation was measured in the Ezeiza station, and is represented as dm water accumulated between consecutive piezometric surveys.

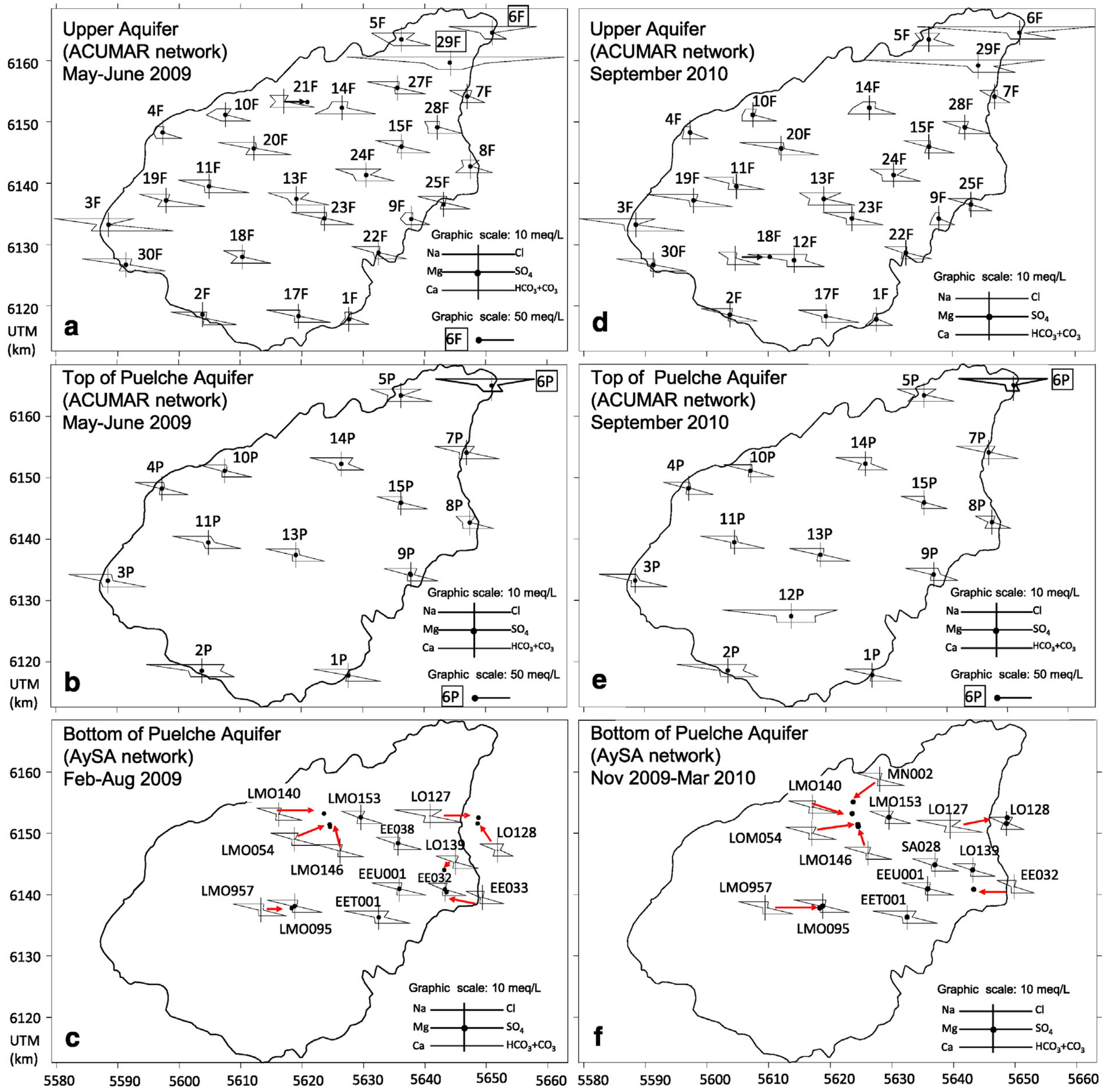

Fig. 3. Stiff diagrams of Upper Aquifer, top and bottom of Puelche Aquifer for two extreme hydrological conditions: low groundwater levels, assumed to represent the driest recorded period (left), and high groundwater levels, assumed to represent the most humid recorded period (right). Arrows in figures c and f indicate the location of the wells.

4.3. Proposed upper limits for groundwater baseline chemistry

As explained in Section 3, in this work the percentile 90 is proposed as upper limit of groundwater baseline composition in the MRB. However, given that both in the Upper Aquifer and in the top of Puelche Aquifer there are a few boreholes in the coastal area which tap connate and/or encroached marine water, the influence of these samples in the 90th percentiles have been evaluated in order to assess the adequacy or not of using them to establish reference values just for the coastal area, but discard them for the rest of the basin.

In the Upper Aquifer, boreholes 6F and 29F are drilled in marine, Postpampeano Sediments which hold saline water. In the top of Puelche Aquifer borehole 6P is also drilled in Holocene marine sediments. The 90th percentile values calculated including data of those boreholes and excluding them are shown in Table 4. As can be observed, to include boreholes 6F, 29F and 6P in the estimation of upper limits for groundwater chemical background produces somewhat higher values for almost all major components, but especially for EC and Cl. Thus, it is advisable not to use them to establish reference values for the whole basin.

5. Discussion

5.1. On groundwater chemical background and proposed upper limits

Groundwater of the Upper Aquifer and of top of Puelche Aquifer has a chemical composition and ranges of concentrations very similar in the major part of the MRB. The samples from AySA wells pumping at the base of Puelche Aquifer in the middle and lower basin also have chemical composition similar to that of groundwater at the top of Puelche Aquifer and at the Upper Aquifer in the same area, but the ranges of contents for the major component are narrower at the bottom of Puelche than in the two upper studied depths. The main cause supporting such similarity of composition is a combination of geology and hydrodynamics: on one hand, the formations that constitute the Upper Aquifer (Pampeano and Postpampeano sediments) and the Puelche Aquifer are mostly sandy and silty siliceous, though the Pampeano and Postpampeano sediments have abundant carbonate layers and nodules; on the other hand, in most of the basin area the dominant hydraulic gradients are vertical downwards, promoting the transference of groundwater from the Upper Aquifer to the Puelche one.

In the Upper and the top of Puelche aquifers the contents of most major components (Cl, SO_4, NO_3, Na, Ca and Mg) range three to four orders of magnitude, which mean that their contents in groundwater are controlled by several processes (mineral dissolution, mixing of different waters, pollution,…). In the same sense, the asymptotic shape of the upper part of the cumulative curves of all those components in the two aquifers indicates that the samples with the largest contents have different solute sources than the rest of the samples. Moreover, the fact that many curves show multi-modal shapes in their upper parts indicate that there are several processes controlling the concentrations of those particular components in the more mineralized samples, the most common pollution and mixing with saline groundwater.

The absence of asymptotic upper ends and multi-modal shapes (except for NO_3) in the cumulative curves of the bottom of Puelche Aquifer means that the gross composition of those samples is controlled by very few processes, mostly mixing of different groundwater flow paths. In fact, in the studied samples of the bottom of Puelche Aquifer (which are spatially concentrated and do not represent the whole basin) the ranges of contents of almost all the components are quite narrow. Considering that the main source of recharge for this aquifer is the Upper Aquifer, the lower variability of the chemical concentrations at this depth should be attributed to the fact that the samples come from exploitation wells, where the flow network patterns should be quite stable, providing groundwater from the same flow lines and in equal proportions.

The asymptotic upper end of Cl, SO_4, Na, Ca and Mg curves in the Upper Aquifer and in the top of Puelche Aquifer should be attributed

Table 3
Summary of statistic values for the studied groundwater samples from the Upper Aquifer and top and bottom of Puelche Aquifer. n: number of samples; St. Dev.: standard deviation; Coef. Var.: coefficient of variation; P: Percentile.

	n	Mean	Median	St. dev.	Coef. var.	Min	Max	P10	P25	P75	P90
Upper Aquifer, ACUMAR network (2008–2011)											
EC (µS/cm)	570	1872	1008	3564	1.9	262	24,400	636	873	1277	2052
pH	568	7.77	7.80	0.44	0.1	6.48	9.40	7.20	7.50	8.00	8.30
Alkalinity (mg/L CO_3Ca)	570	510	475	183	0.4	106	1190	307	406	562	704
Cl (mg/L)	570	268.0	23.0	984.0	3.7	4.0	6540.0	9.0	12.0	65.0	216.5
SO_4 (mg/L)	567	115.6	23.0	455.5	3.9	2.0	3295.0	10.0	14.0	46.0	78.0
NO_3 (mg/L)	545	28.5	13.0	35.1	1.2	1.6	230.0	6.0	8.0	32.0	77.0
Na (mg/L)	570	329.9	183.0	709.1	2.1	12.0	4970.0	47.5	108.0	232.0	345.5
K (mg/L)	570	20.1	16.0	16.7	0.8	7.0	130.0	11.0	12.0	18.8	36.0
Ca (mg/L)	570	65.4	44.0	86.0	1.3	6.0	929.0	16.0	24.0	76.0	117.5
Mg (mg/L)	570	32.0	17.0	57.1	1.8	1.0	546.0	6.0	10.0	32.0	54.0
As (mg/L)	548	0.03	0.02	0.03	0.9	0.01	0.16	0.01	0.01	0.03	0.06
Fe (mg/L)	130	0.31	0.03	0.89	2.9	0.01	7.80	0.01	0.03	0.05	1.06
Mn (mg/L)	130	0.08	0.03	0.35	4.7	0.02	3.50	0.02	0.03	0.03	0.05
Cu (mg/L)	130	0.02	0.00	0.02	1.4	0.00	0.11	0.00	0.00	0.03	0.03
Zn (mg/L)	106	0.02	0.01	0.02	1.2	0.00	0.14	0.00	0.00	0.02	0.04
NH_3 (mg/L)	561	0.11	0.03	0.76	7.0	0.03	12.00	0.03	0.03	0.03	0.09
NO_2 (mg/L)	494	0.02	0.01	0.04	2.4	0.01	0.61	0.01	0.01	0.01	0.02
Total N (mg/L)	554	6.88	3.21	10.09	1.5	0.01	143.60	1.41	1.86	7.28	18.12
Top of Puelche Aquifer, ACUMAR network (2008–2011)											
EC (µS/cm)	322	1756	1094	2040	1.2	256	10,300	819	895	1360	2810
pH	320	7.92	7.90	0.42	0.1	6.86	9.00	7.40	7.60	8.20	8.45
Alkalinity (mg/L CO_3Ca)	322	493	466	141	0.3	105	1000	361	420	530	602
Cl (mg/L)	322	216.0	35.0	552.8	2.6	6.0	2500.0	11.4	15.0	74.0	459.0
SO_4 (mg/L)	322	108.0	45.0	151.2	1.4	6.0	666.0	15.0	29.0	88.0	347.0
NO_3 (mg/L)	293	40.1	15.0	61.1	1.5	2.0	271.0	5.0	6.0	40.0	124.0
Na (mg/L)	322	352.6	232.5	420.2	1.2	43.0	2060.0	168.0	202.0	273.0	457.0
K (mg/L)	322	15.1	12.0	9.8	0.7	7.2	60.0	9.3	10.0	16.0	21.0
Ca (mg/L)	322	43.4	27.0	39.2	0.9	9.0	240.0	16.0	19.0	48.0	104.0
Mg (mg/L)	322	20.4	11.0	30.3	1.5	1.0	273.0	4.3	7.0	19.0	43.0
As (mg/L)	304	0.03	0.02	0.02	0.71	0.01	0.13	0.01	0.01	0.04	0.06
Fe (mg/L)	70	0.25	0.03	0.78	3.08	0.03	5.60	0.03	0.03	0.07	0.44
Mn (mg/L)	70	0.06	0.03	0.14	2.53	0.02	1.13	0.02	0.03	0.03	0.04
Cu (mg/L)	70	0.01	0.01	0.01	0.82	0.00	0.04	0.00	0.00	0.03	0.03
Zn (mg/L)	55	0.01	0.01	0.01	1.12	0.00	0.05	0.00	0.00	0.01	0.03
NH_3 (mg/L)	307	0.10	0.03	0.46	4.50	0.03	4.50	0.03	0.03	0.03	0.09
NO_2 (mg/L)	278	0.04	0.01	0.15	3.85	0.01	1.53	0.01	0.01	0.01	0.04
Total N (mg/L)	314	8.94	3.21	13.75	1.54	0.01	61.24	1.18	1.41	8.70	27.60
Bottom of Puelche Aquifer, AySA network (2003–2010)											
EC (µS/cm)	115	922	849	251	0.3	417	1550	685	734	982	1385
pH	115	7.76	7.80	0.15	0.0	7.30	8.20	7.60	7.70	7.80	7.90
Alkalinity (mg/L CO_3Ca)	115	398	389	73	0.2	96	530	340	350	447	490
Cl (mg/L)	115	32.5	22.0	27.7	0.9	8.6	124.0	10.1	12.3	41.1	86.7
SO_4 (mg/L)	115	25.5	13.5	25.3	1.0	4.1	116.0	5.0	6.3	31.9	77.4
NO_3 (mg/L)	115	26.2	17.3	26.5	1.0	2.0	119.0	3.4	12.2	32.7	51.3
Na (mg/L)	115	175.0	170.0	50.6	0.3	45.0	310.0	120.0	130.0	200.0	250.0
K (mg/L)	115	9.2	8.6	2.3	0.2	4.1	17.0	6.7	7.8	10.0	13.0
Ca (mg/L)	115	19.7	17.0	7.0	0.4	11.0	46.0	13.0	15.0	23.0	28.0
Mg (mg/L)	115	11.0	9.3	5.1	0.5	6.0	45.0	6.8	8.2	13.0	18.0
As (mg/L)	112	0.04	0.04	0.01	0.30	0.01	0.09	0.02	0.03	0.04	0.05

to mixing with saline water from Holocene marine sediments in the Upper Aquifer, and from Holocene marine ingressions in the Puelche Aquifer. Thus, marine water is present in both aquifers in the lower basin. The asymptotic upper end of the NO_3 curve must be related to pollution. As already said, it was surprising to find that most of the samples in the Puelche Aquifer have significant contents of NO_3, with maximum values comparable to those of the Upper Aquifer. In both aquifers the major contents of NO_3 are found in the middle and especially in the lower basin, where there is not agriculture but a dense population with incomplete sewage coverage, thus the pollution source for NO_3 must be wastewater. The fact that samples from the top of Puelche Aquifer have similar nitrate levels than the Upper Aquifer (around 270 mg/L) means that there is some mechanism allowing a rapid transfer of groundwater from the Upper Aquifer downwards. The most probable mechanism is enhanced vertical groundwater flow in the middle and lower basin, induced by concentrated and intensive abstraction of groundwater in the lower part of the Puelche Aquifer since the middle of the last century. The existing piezometric drawdown may even induce flow of polluted groundwater from the Upper Aquifer to the Puelche one through the annular space of deep boreholes.

Wastewater would probably incorporate also Cl, SO_4, Na and other major, minor and trace solutes to groundwater, but looking to the shapes of their cumulative curves in the Upper Aquifer it seems that the possible contribution of those solutes is surpassed by the mixing with old marine water. The multi-modal curves of the top of Puelche Aquifer samples could be related to pollution, but considering that i) those samples come from boreholes screened at different depths in a confined to semi-confined aquifer, and ii) two boreholes in the upper basin also provide saline water, but as a result of mixing with groundwater from the underlying Paraná Formation (a marine water much older and chemically evolved than this one in the coastal zone of the lower basin), it is unprovable that the modes of those curves are due to pollution processes. They most probably obey to the spatial heterogeneity of mixing process with saline water of different origins and compositions.

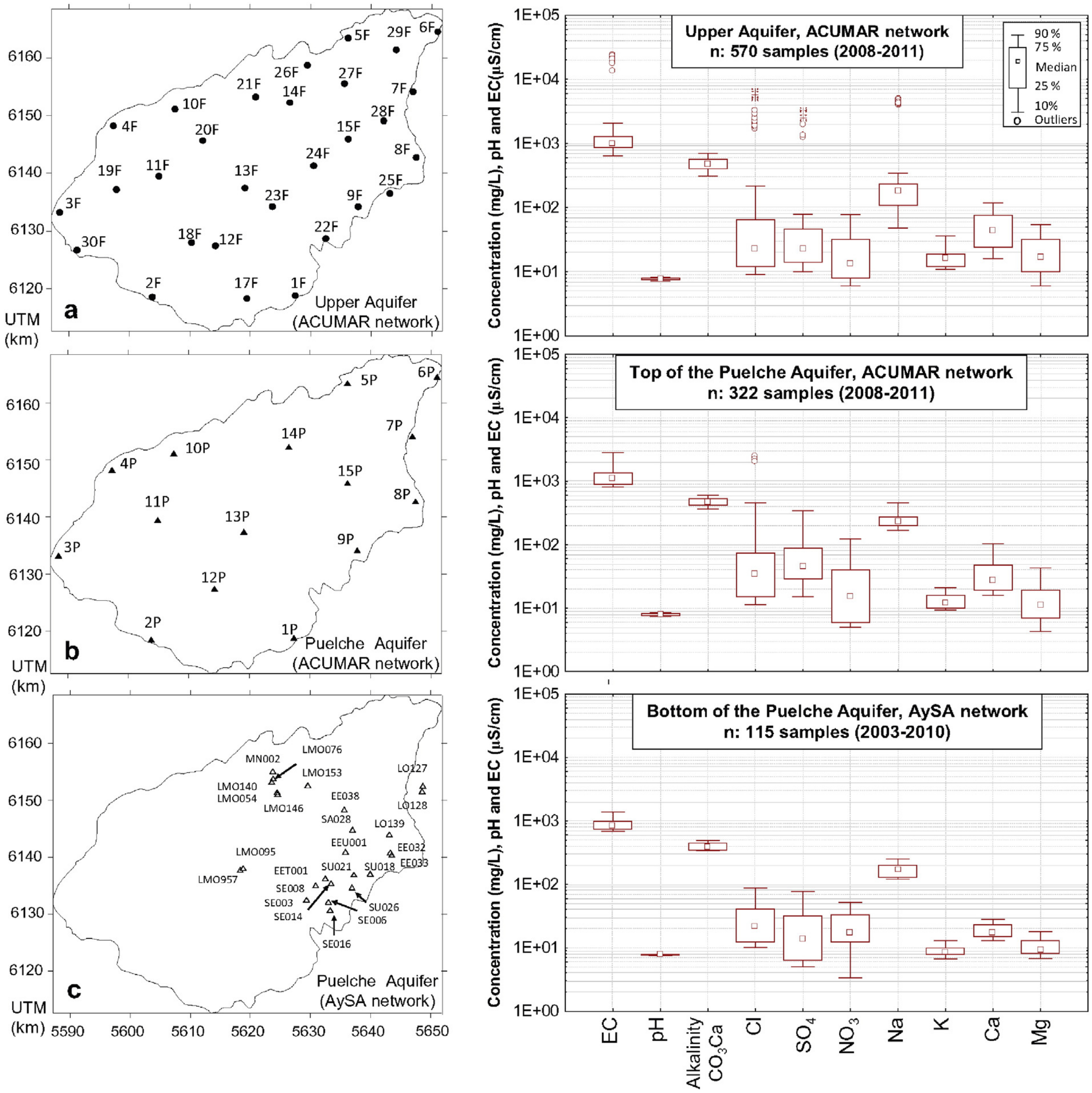

Fig. 4. Left: Location of the ACUMAR boreholes and AySA wells used for the study. Right: Boxplot of statistical values for EC, pH and major chemical components in the Upper Aquifer, top and bottom of Puelche Aquifer. Solute concentrations are in mg/L, and EC in µS/cm. Arrows in figure c indicate the location of the wells.

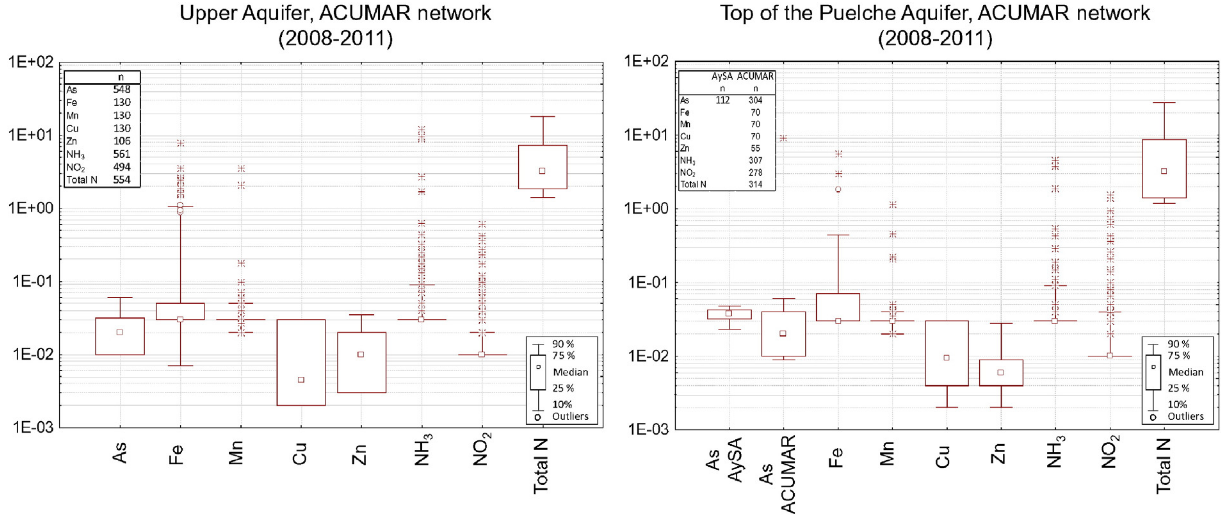

Fig. 5. Box plots of statistical values for As in the Upper Aquifer, top and bottom of Puelche Aquifer, and for Fe, Mn, Cu, Zn, NH_3, NO_2, and total N in the two first aquifer layers (in the bottom of Puelche Aquifer they were reported under the detection limit). Concentrations are in mg/L.

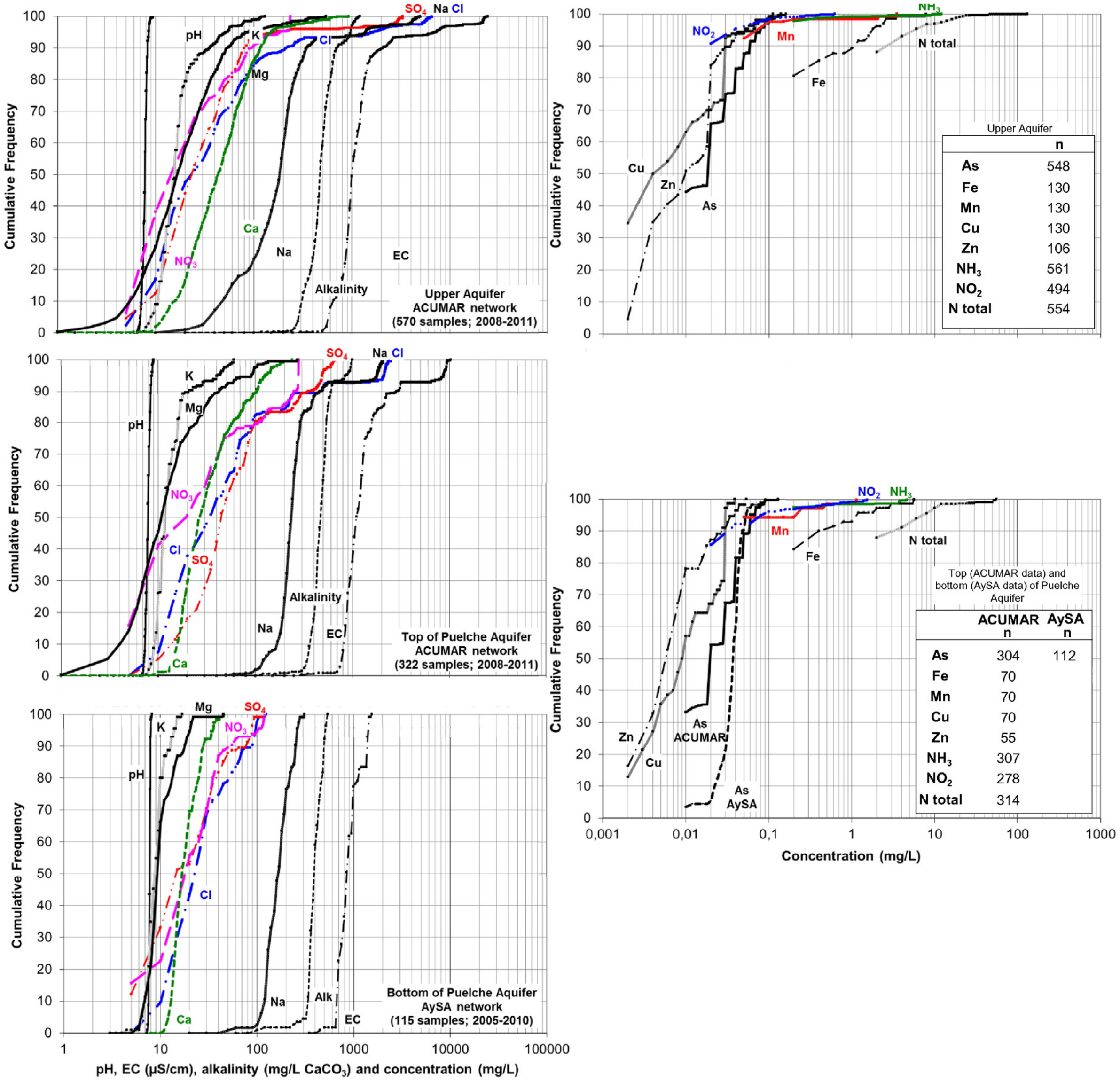

Fig. 6. Cumulative probability plots of the concentrations of major, minor, and trace components, and of EC values in the Upper Aquifer, top and bottom of Puelche Aquifer.

The most abundant component in the majority of the samples of the two studied aquifers and the three depths is alkalinity, which corresponds mostly to HCO_3. In fact, the ranges of values and statistical medians of alkalinity are practically identical in the three studied depths. There are two main sources of alkalinity in the MRB, and both are located in the Upper Aquifer: dissolution of CO_2 during water infiltration and, quantitatively more relevant, dissolution of $CaCO_3$. Carbonate dissolution is prompted by another relevant reaction: cation exchange, which uptakes Ca (more than Mg) and release Na (Manzano et al., 2015). Because of these two reactions Na is the second more abundant component after alkalinity in the major part of the samples of the two aquifers. The fact that the range of Na contents decreases with increasing depth suggest that the cation exchange process is active only – or mostly – in the Upper Aquifer, as has also been observed in other basins (Zabala et al., 2015). The range of alkalinity contents is practically the same in the three aquifer depths because groundwater reaches equilibrium with calcite already in the Upper Aquifer (Manzano et al., 2015). Those two reactions also control the range of pH values, which like alkalinity, are very similar in the three aquifer depths. Finally, the fact that pH and alkalinity do not have outlier values in Fig. 4 supports the hypothesis that both variables are controlled by very few processes in the three aquifers, and that occurrence of these processes is fairly homogeneous across the basin.

With respect to the dominant chemical facies, in the major part of the MRB and at the three studied aquifer depths (Upper Aquifer, top and bottom of Puelche Aquifer) groundwater has Na-HCO_3 chemical facies. This facies results from the main – from a quantitative point of view – hydrogeochemical processes taking place in the Upper Aquifer during and shortly after recharge: cation exchange, with Ca uptake and Na release, and $CaCO_3$ dissolution (Manzano et al., 2015), which is also consistent with the results of other authors in other basins (Heredia et al., 2003; Carol et al., 2012). The observation that Na-HCO_3 waters are not influenced neither by dilution of increased recharge in humid periods nor by evapotranspirative concentration in dry periods, means that those waters are quite evolved from the chemical point of view. This is somewhat surprising for the samples of the Upper Aquifer, which were expected to change notably during recharge episodes. The generalized lack of changes may obey to the fact that the samples from the Upper Aquifer are not from the phreatic zone, but somewhat deeper (see position of screens in Table 1), where they are already evolved chemically. It may also obey to the fact that the samples are from areas of relatively slow groundwater recharge, which would allow time to modify relative cation abundances because of cation exchange.

The few samples of the Ca-HCO_3 type found in the Upper Aquifer are associated to recently recharged groundwater, with the cation abundances not yet modified by cation exchange, while the two samples with Na–Cl facies found in the lower basin are associated to mixing of locally recharged water with connate marine in the Postpampeano Sediments (Manzano et al., 2015). All the Upper Aquifer samples with Ca-HCO_3 and Na–Cl facies show some compositional changes with recharge and drying conditions: in Ca-HCO_3 samples, the relative abundances of Ca and Mg change with recent recharge (humid periods) but their global mineralization does not change, pointing to cation exchange processes as the main cause. The Na–Cl samples dilute notably in humid periods with respect to dry ones, though the chemical facies does not change.

The fact that groundwater in the Puelche Aquifer has the chemical signature of the Upper Aquifer in most of the MRB area suggest that the vertical transfer of water from the Upper to the Puelche aquifers must occur on a broad spatial scale. However, two boreholes in the upper basin (2P and 12P) have Na-ClSO_4 facies, which is associated to mixing of originally Na-HCO_3 water with saline (probably Na-Cl, but may be Na-Cl–SO_4) water from the underlying Paraná Formation. This is a main result from a study recently performed but not yet published (Manzano et al., 2015). Another borehole has Cl–Na water, but it is located in the coastal area (6P) and its salinity obeys to the fact that the borehole is drilled in marine sediments. Given that the borehole goes across clayey silts and clays and is screened between 25 and 28 m depth, the small chemical dilution observed in the studied humid period could be due to preferential infiltration of freshwater through the borehole annular space. The mixing of locally recharged groundwater with marine water encroached in the Puelches Formation has been proposed by other authors for this basin (Auge, 2004) and for La Plata area, to the E of the MRB (Logan and Nicholson, 1998; Logan et al., 1999); the possible local existence of mixing with saline water from the underlying Paraná Formation has been proposed by Auge (2004).

Table 4
Values of the 90th percentile of major chemical variables and EC values in the Upper Aquifer and top Puelche Aquifer calculated including and excluding data from the coastal, saline boreholes 6F, 29F and 6P.

Upper Aquifer, ACUMAR network (2008–2011)

	Excluding boreholes 6F and 29F		Including boreholes 6F and 29F	
Parameter	n	90th percentile	n	90th percentile
EC (μS/cm)	139	1396	144	1637
pH	139	8.30	144	8.30
Alkalinity (mg/L CO_3Ca)	139	675.0	144	680.0
Cl (mg/L)	139	48.8	144	115.0
SO_4 (mg/L)	137	42.0	142	45.0
NO_3 (mg/L)	126	9.0	127	9.0
Na (mg/L)	139	318.0	144	327.0
K (mg/L)	139	22.0	144	27.0
Ca (mg/L)	139	78.3	144	84.0
Mg (mg/L)	139	28.0	144	30.0

Top of Puelche Aquifer, ACUMAR network (2008–2011)

	Excluding borehole 6P		Including borehole 6P	
Parameter	n	90th percentile	n	90th percentile
EC (μS/cm)	94	1270	96	1282
pH	94	8.60	96	8.60
Alkalinity (mg/L CO_3Ca)	94	604.0	96	604.0
Cl (mg/L)	94	49.0	96	49.0
SO_4 (mg/L)	94	90.0	96	98.0
NO_3 (mg/L)	82	8.0	83	8.4
Na (mg/L)	94	281.0	96	286.0
K (mg/L)	94	16.0	96	16.4
Ca (mg/L)	94	31.0	96	32.0
Mg (mg/L)	94	15.0	96	16.0

All the samples from AySA wells pumping the base of Puelche Aquifer in the middle and lower basin have Na-HCO_3 facies and a very stable chemical composition, with very subtle temporal changes not related to hydrological changes but to pumping management (Manzano and Zabala, 2012). As proposed above, the great temporal stability of those samples is most probably due to the fact that they come from exploitation wells. However, it should be taken into account that the chemical composition of those samples does not represent the whole basin area, and different facies may appear in other zones.

Considering the influence of geology on groundwater quality, particularly the existence of Holocene marine water in the coastal sectors of the Upper Aquifer and top of Puelche Aquifer, two values are proposed as upper limit of the natural baseline for both aquifer layers. In both aquifers, the inclusion of boreholes drilled in marine sediments and continental sediments affected by marine ingression (boreholes 6F and 29F in the Upper Aquifer, and 6P in the Puelche one) increases somewhat the upper value of some major components, though not significantly (see Table 4): in the Upper Aquifer, the 90th percentile of EC, Cl, SO_4, Na, K, Ca y Mg is a little bit larger considering boreholes with saline water that not considering them; in the top of Puelche Aquifer only EC, SO_4 and Na are somewhat higher. Thus, it has been considered reasonable to propose different upper limits for the coastal area of both aquifers and for the rest of them. Given that the samples available from the bottom of Puelche Aquifer do not cover the whole basin area, it is not reasonable to propose upper baseline limits for this aquifer level.

Despite the relative low density of the monitoring network at the time when the study was performed, the results of this work are considered useful for a preliminary investigation, and representative of the real conditions across the basin. This is based in the homogeneity of groundwater chemical composition in most of the basin and in other basins nearby, in the fact that chemical differences appear concentrated in the coastal zone and in the upper basin, and in the analysis of the six years chemical data series available from the ACUMAR monitoring program. Moreover, ACUMAR enlarged the groundwater monitoring network to 86 boreholes in 2014 and to 91 in 2015. The new, recent data available reproduce those used in this work, and the baseline ranges and upper limits under review do not differ significantly from the ones presented here. Thus, the results of this work provide a baseline hydrochemical scenario of the investigated area suitable to implement water resource management actions, which should include a more refined monitoring network at smaller scale in areas of nitrate pollution and groundwater salinization.

5.2. On the implications for aquifer management

Groundwater is used in the basin as complementary water supply source, and as the only source for all demands in those areas where supplying with water imported from Río de la Plata is not available. The essentially urban use has led that water companies dominate the groundwater management. In this way, the objective of the water quality has been limited to the current uses, and the monitoring purposes to control the standards for drinking water quality.

For ACUMAR, the design and implementation of an integrated management plan in the basin has the objective of recovery and protection of water quality, in order to prevent damages to human health and the environment. In this instance, management acquires a new dimension, and the need to establish natural baseline levels of groundwater arises for surveillance and monitoring purposes, focusing in evaluating to what extent the system has been affected by human activities, taking a yardstick for detecting deterioration of groundwater quality and also a reference for restoring water quality.

In the context of the existing recovery plan, ACUMAR coordinates with the water companies in the basin the necessary works to expand the coverage of water supply and sanitation services. From year 2010, 0.9 and 1.3 million inhabitants were connected to sewage and drinking water services, respectively (ACUMAR, 2014). Nitrate contamination, principally from on-site sanitation systems, is the most common and more widely accepted cause of negative trends in groundwater quality, so it is expected that these actions produce changes in the trends, which should be assessed with an acceptable level of reliability. The existence of a simple indicator into ACUMAR indicators system (ACUMAR, 2014) to evaluate the NO_3 concentration is useful to simplify and communicate the progress in the objectives of PISA. However, understanding how and where the changes occur is necessary for monitoring the effects of the actions performed.

The expansion of water supply and sanitary services also brings modifications into the hydrodynamic conditions of the aquifers, due to changes not only in the inputs and outputs of water from sanitation systems, but also from changes in the water supply sources and in their chemical composition (groundwater to surface water, and/or individual extraction boreholes to wellfield). A key issue to consider in the monitoring activities is the influence of mixing processes on the groundwater quality both in the lower and the upper zones of the basin, as supply wells in both areas may eventually increase their salinity due to mixing with saline water prompted by the pumping.

For the purposes of ACUMAR, the natural baseline of groundwater is also a useful standard for assessing the impact of land use changes in the aquifer quality, for example where highly polluting activities are being displaced and/or converted (such as tanneries in Lanus district, in the lower basin), or where new industrial activities are being installed (especially in the upper basin).

Additionally, there is also a need to characterize the groundwater quality taking into account the importance of its contribution to the river quality through the base flow. A target of quality on the river has been established by ACUMAR, so reaching this target requiresto know the base flow quality contributing to the river and its possible spatial and temporal variations.

ACUMAR is the prevalent authority in environmental issues in the basin ambit, so once background levels are established, an initial, reference condition for monitoring is defined. To set this reference requires not only of a process of scientific evaluation, but also of agreements between different agencies of the three political jurisdictions having liabilities in the MRB, so ACUMAR is working in this way.

6. Conclusions

In the context of the Integrated Environmental Sanitation Plan in the Matanza- Riachuelo River basin, a hydrochemical study has been performed to identify the existing groundwater chemical facies and the processes originating them, to establish the variation ranges for the physical and chemical variables evaluated, and to propose upper limit values for the baseline composition.

Based on the study of 1007 groundwater samples from three aquifer layers (Upper Aquifer — siliceous and carbonated Postpampeano and Pampeano Sediments; top and bottom of Puelche Aquifer —siliceous Puelches Formation), most of the groundwater in the three layers is Na-HCO_3 type, except a few Ca-HCO_3 samples in the Upper Aquifer; some Na-Cl samples in the coastal zone of both the Upper Aquifer and the top of Puelche Aquifer, and two Na-$ClSO_4$ samples at the top of Puelche Aquifer in the upper basin.

The Ca-HCO_3 waters own their composition mostly to the dissolution of gases and carbonate minerals during recharge. The Na-HCO_3 waters, which are the most abundant across the basin, own their composition mostly to cation exchange and carbonate dissolution. The Na-$ClSO_4$ samples from the top of Puelche Aquifer in the upper basin own their composition to the mixing of Na-HCO_3 water with Na-Cl pore water from the underlying marine sediments of the Paraná Formation. The Na-Cl waters in the Upper Aquifer and lower basin own their composition to the mixing of Na-HCO_3 water with connate Holocene marine water of the marine Postpampeano Sediments. The Na-Cl waters in the top of Puelche Aquifer in the lower basin own their composition to the mixing of Na-HCO_3 water with Holocene marine water intruded in the coastal area of the Puelches Formation.

All the chemical facies maintain in the two different hydrological periods analysed (dry season, with the lowest recorded levels, and wet season, with the highest recorded levels) and at the three depths studied. This suggests that changes in the recharge/evapotranspiration balance are not the main factor controlling groundwater chemical composition, even in the Upper Aquifer. However, the shallowest samples studied in this aquifer are not from the phreatic zone but deeper, and this may be the cause of the observed absence of seasonal changes.

The median values and the variation ranges of most of the chemical components are similar in the Upper Aquifer and in the top of Puelche Aquifer due to the hydraulic connection of both layers, and to the low reactivity of the Puelche mineralogy. At the bottom of Puelche Aquifer, both the median values and the variation ranges of all the components are smaller than in Upper and top of the Puelche aquifers due to the origin of the samples: exploitation wells spatially concentrated (not covering the whole basin) and providing groundwater from the same flow lines and in similar proportion (stable mixture) along time.

With respect to NO_3, many samples in the three aquifer layers have concentrations well above 10 mg/L (maximum limit considered of natural origin). The source of NO_3 in the Puelche Aquifer is the Upper Aquifer. In the middle and lower sectors of the basin, the existence of vertical downward hydraulic gradients (increased and/or induced by pumping) accelerated the transport of wastewater-polluted groundwater from the Upper to the Puelche aquifers. The contribution to pollution of preferential flow through the annular space of the exploitation wells may be relevant, but it has not been studied.

Taking into account the influence of geology and marine paleo ingressions in groundwater chemistry, two upper limits are proposed for the chemical baseline in the Upper Aquifer and in the top of the Puelche Aquifer. For each aquifer, one of the limits applies to groundwater in the coastal fringe, where there are saline waters, and the other applies to the rest of the basin.

This study allowed to know the initial chemical conditions of the groundwater system of the Matanza-Riachuelo River basin and to establish the reference values from which ACUMAR can start to evaluate trends and monitoring the recovery plan. Most probably, in a near future Argentina, and the rest of Latin American countries as well, would have to implement regulations about groundwater quality in order to protect and recover water resources, and thereby to prevent damage to human health and the environment. Those regulations will require knowledge of the natural groundwater composition in order to understand the origin of groundwater chemistry and quality to discriminate natural and anthropically modified chemical conditions, and to establish reference values for recovery actions. This work intends to be a reference for those future studies.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, http://dx.doi.org/10.1016/j.scitotenv.2015.10.006. These data include the Google map of the most important areas described in this article.

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