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ORIGINAL ARTICLE

Hydrochemical and isotopic characterization of the hydrological budget of a MAB Reserve: Mar Chiquita lagoon, province of Buenos Aires, Argentina

Melisa Glok Galli · Daniel Emilio Martínez · Eduardo Emilio Kruse · Sebastián Iván Grondona · María Lourdes Lima

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Abstract Mar Chiquita is a coastal lagoon located in the Argentine Buenos Aires province in South America. The aim of this study was to perform a hydrochemical and stable isotopes characterization in order to better the understanding of the hydrology of the Mar Chiquita lagoon's catchment and its water budget. Groundwater samples were taken from 144 wells and 21 samples from main streams, and seven lagoon water samples were also collected. Chemical analyses were carried out using standard laboratory methods, and isotopic determinations were made through laser spectroscopy using a DLT-100 liquid–water isotope analyzer. Hydrochemical analysis permits a general classification of groundwater and streamwater as sodium bicarbonate waters, while the lagoon chemical composition shows an evolution toward seawater composition, from the north to its mouth, which is located southerly. Isotopic data show a source of aquifer recharge from rainfall and a groundwater domain into the streams' flow. Three main components can be recognized as end members in a plot of electrical conductivity (EC) versus δ^{18}O: seawater, streamwater and groundwater. Obtained EC values for groundwater in the discharge zone (EC average value = 3,516 µS/cm) allow minimizing its direct contribution and to take into consideration two dominating end members: streamwater and seawater. Mar Chiquita lagoon's water falls close to the line between streamwater and seawater end members according to its EC and δ^{18}O. The obtained seawater proportion for these samples ranges from 84 % in the lagoon's mouth to around 0 % in the more distal area.

Keywords Mar Chiquita lagoon's catchment · Hydrochemistry · Isotope hydrology · Hydrogeochemical modeling · Hydrological budget

Introduction

Groundwater is the main supply source for urban, agricultural and industrial use in the southeastern Buenos Aires province of the Argentine Republic (Fig. 1). Surface water is an active component within the groundwater flow system (Winter 1999). Streams, which are not significant regarding supply, are an important part of the hydrological dynamics in this area. Wetlands, as part of the hydrological system, provide significant environmental services, such as a nutrients cycle contribution, local and regional climate regulation, hydrological flows regulation, and educational and recreational possibilities, just to name a few (MA 2005).

Mar Chiquita lagoon, in the coastal area of the southeastern Buenos Aires province, is an important wetland for biodiversity sustainability. In April 1996, UNESCO, through its Man and the Biosphere program (MAB),

M. Glok Galli (✉) · D. E. Martínez · E. E. Kruse · S. I. Grondona · M. L. Lima
Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Buenos Aires, Argentina
e-mail: glokgalli@mdp.edu.ar

M. Glok Galli · D. E. Martínez · S. I. Grondona
Instituto de Investigaciones Marinas y Costeras (IIMyC), CONICET-Universidad Nacional de Mar del Plata (UNMDP), Funes 3350, 7600 Mar del Plata, Argentina

M. Glok Galli · D. E. Martínez · S. I. Grondona · M. L. Lima
Instituto de Geología de Costas y del Cuaternario (IGCyC), UNMDP, Casilla de Correo 722, 7600 Mar del Plata, Argentina

E. E. Kruse
Facultad de Ciencias Naturales y Museo, Universidad Nacional de La Plata (UNLP), Calle 60 y 122, 1900 La Plata, Argentina

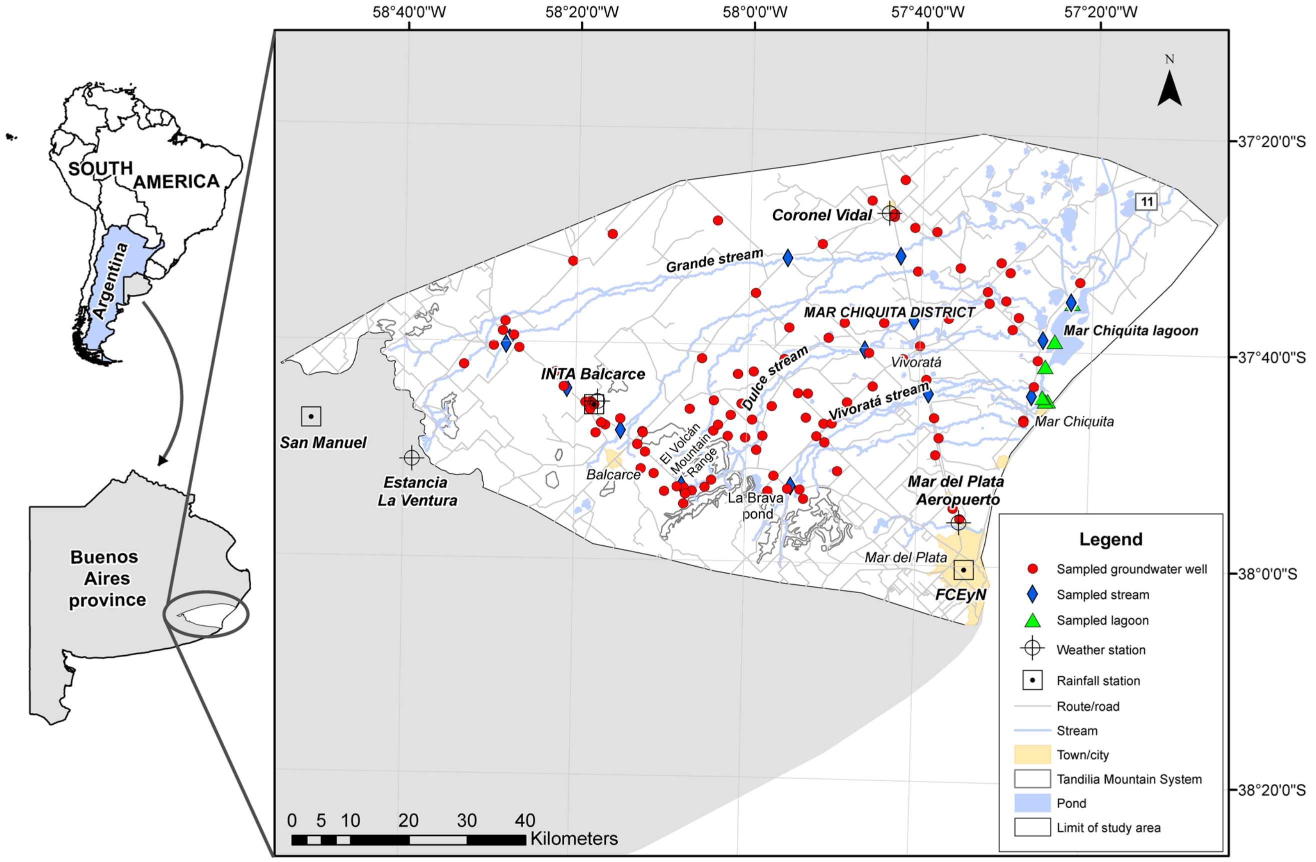


Fig. 1 Location map, sampling sites, and weather and rainfall stations

declared the lagoon and surroundings as one of its global MAB Reserves. The Biosphere Reserve concept was developed as a necessity to establish regional sustainable development strategies (Iribarne 2001). In February 1999, the Provincial Government declared this area as a Multiple Use Nature Reserve called "Mar Chiquito Atlantic Park" (Mangiarotti and Cañete 2002). The MAB Reserve is limited in the west by the Provincial Route 11, in the north by the Mar Chiquita district and in the south by the Mar Chiquita town, which occupies an area of 26,488 ha (Fig. 1).

According to its hydrodynamics, it can be divided into a freshwater zone, characterized by continental water discharge without tidal effects, and an estuarine zone, located from the mouth to the effective limit of tidal influence. The boundary between both freshwater and estuarine zones is highly variable, defined by a combination of parameters such as tidal range, weather conditions and freshwater volume in the lagoon (Martos and Reta 1997).

The hydrochemical interpretation of representative water samples analyses is a useful tool in the analysis of hydrological systems. It allows determining different types of waters, interaction and mixing between them and possible modifying processes along flow lines, due to varied analysis of ionic species (Martínez et al. 2000; Wang et al. 2006). Moreover, the use of environmental isotopes for groundwater dynamics study in hydrological systems is of utmost interest. Physical processes and weather phenomena, responsible both for water transport in the different hydrological cycle phases, produce an isotopic fractionation that can be used to obtain conclusions about its source and behavior. In this way, isotopic determinations may have a number of further applications such as recharge and discharge estimations, groundwater–surface water interactions and water residence times in aquifers, among others (Clark and Fritz 1997; Cook and Herczeg 1999; Geyh 2000).

Little information regarding hydrochemical composition data in the Mar Chiquita lagoon has been reported. Marcovecchio et al. (2006) evaluated the spatial and seasonal variations in eight hydrographical parameters (temperature, salinity, nitrate, nitrite, phosphate and silicate in water, chlorophyll *a* and phaeopigments content in suspended particulate matter), identifying two completely different hydrographical areas within the coastal lagoon. One of these zones shows a marine influence, while the other is dominated by inland influence (due to catchment and freshwater inputs); both bearing different characteristics and ecological behavior. The authors further argue that freshwater influence is more significant than that of seawater. They also concluded that the lagoon's main input is the continental drainage, which collects rain water from a large basin, including the Tandilia Mountain System. Nevertheless, the possibility of groundwater contribution was not taken into account in this paper (Marcovecchio et al. 2006).

Freshwater discharge into a lake can be done through streams or also by direct groundwater discharge. On one hand, direct groundwater discharge is difficult to quantify. On the other, the baseflow proportion in the streamwater discharge may not be properly considered. Stable isotopes studies on a different catchment in the same geographical region (Martínez et al. 2007) estimate that streamwater is formed by about 80 % of baseflow. Previous studies have not been focused to establish groundwater flow and discharge on a regional scale in the case of the Mar Chiquita lagoon's catchment. Despite that, specific surveys have been carried out on water bodies present in the catchment source area (Romanelli et al. 2010).

This study's aim is to perform a hydrochemical and stable isotopes characterization in order to better the understanding of the hydrology of the Mar Chiquita lagoon's catchment and the lagoon water budget. This could be an important conceptual issue for future hydraulic balances and future freshwater discharge quantification.

Some contributions exist as background related to many of the aspects that must be considered. Sala (1975, 1977) established the main features of the hydrogeology of the Buenos Aires province. Fasano (1980) performed the first hydrogeological characterization of the catchment, and Kruse (1986) analyzed the hydrology of the Vivoratá creek. Iribarne (2001) published a book that includes many of the main issues related to the MAB Reserve, mostly focusing on ecological and environmental matters. Levin et al. (1988) generated the first stable isotopes data. Main hydrogeological and hydrochemical processes in the Pampeano aquifer in the southeastern Buenos Aires province were described by Massone (2000), Martínez and Bocanegra (2002) and Lima et al. (2013). These previous studies did not estimate the hydrological budget of the lagoon.

Description of the area

Mar Chiquita is a coastal lagoon with a length of 25 km and a width varying between 100 and 4,500 m. It covers a total area of 46 km^2 with a tributary catchment of 10,000 km^2 (Fasano 1980). Its shape is irregular, reaching a maximum depth of 1.50 m, its bottom topography being very smooth (Lanfredi et al. 1981). The lagoon is connected to the sea through an elongated inlet channel of approximately 6 km length and more than 200 m in width (Marcovecchio et al. 2006). It could be possible then to find flora and fauna of different subenvironments. Furthermore, the lagoon receives discharge from the Grande, Dulce and Vivoratá streams, among others, whose sources are in the ranges belonging to the Tandilia System (Fig. 1). These creeks flow through most of their course at very low gradient environment known as Depressed Pampa (Tricart 1973). The Tandilia Mountain System is located in the catchment's more western section and is surrounded by a zone of hills and fluvial–eolian plain, which ends on a seafront which extends approximately 50 km. According to its dominant topographic features, it is possible to recognize in the study area three defined zones: mountain ranges, hills and plain. The relief is only slightly marked, varying in height from 2.34 meters above sea level (masl) to 360 masl (Lima et al. 2013).

The mountain range has dominant slopes of about 5 % and steeper ones of more than 20 %. The hills appear in a piedmont environment, with gradients of about 2–3 % in the northeast and with slopes of about 2 % in the south. Toward the plain environment, regional gradients of approximately 0.2–0.3 % were observed northward, while values ranging between 0.3 and 0.7 % were found southward (Kruse 1986). On a more local scale, toward the lagoon, the gradient is very low, between 0.01 and 0.015 % (Tricart 1973). The climate of the area is "temperate-humid" according to the Köppen classification, or "sub-humid mesothermal, without deficiency of water" according to the Thornthwaite method (Kruse 1986).

Based on drilling lithological description, field work and the proposal of Sala (1977), it is possible to recognize the presence of an impermeable basement in the study area, formed by Precambrian basement rocks and Eopaleozoic orthoquartzites of the Balcarce Formation (Dalla Salda and Iñiguez 1979). Moreover, the "Epiparaniana section," identified by Sala (1975) (Massone et al. 2005), is the most important sequence from a hydrogeological point of view because it is part of the principal aquifer of the area, the Pampeano aquifer (Martínez and Bocanegra 2002). Basement quartzites form a set of tectonic graben and horst dividing some compartments and making the detrital aquifer discontinuous along the coastal area of Mar del Plata.

The aquifer sometimes lies directly over the Balcarce Formation and others over the Miocene deposit of marine green clays of the Paraná Formation (compounding the "Paraniana section" of Sala 1975). It consists of Pampeano sediments "sensu strictu" (Pleistocene-Holocene) and also Holocene loessic sediments known as Post-Pampeano sediments (Fig. 2). Its thickness can vary from a few meters to more than 100 m, and its grain size is variable,

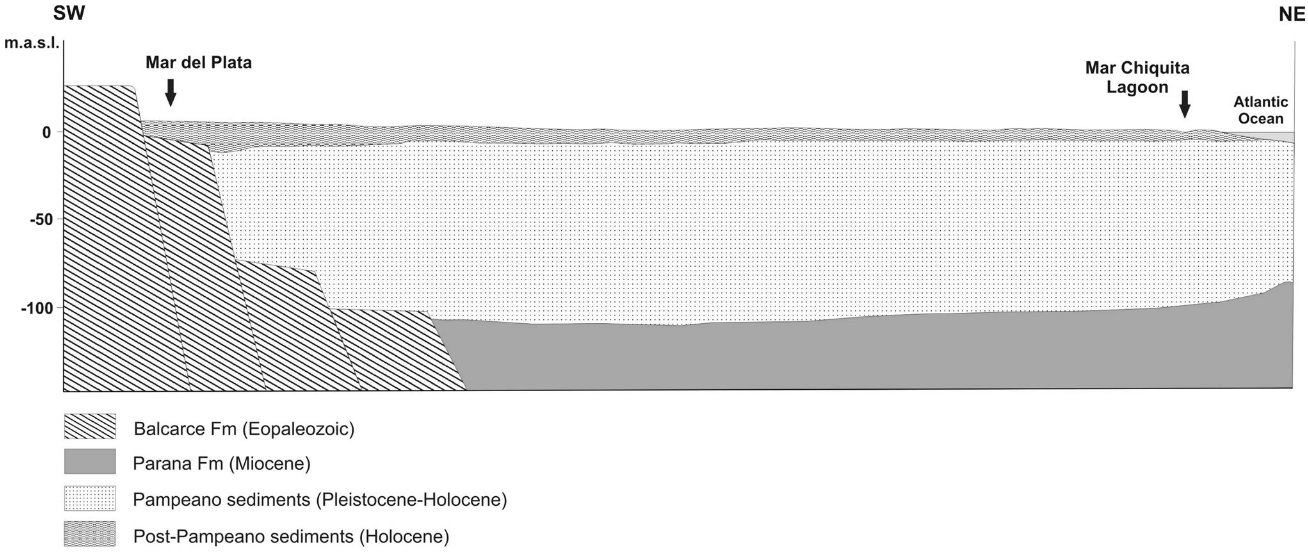


Fig. 2 Schematic geological section of the study area

between sand and silt and with clay intercalations. This is considered an “unconfined and multi-layer” clastic aquifer (Martínez and Bocanegra 2002). Levels of “tosca” or powdered $CaCO_3$ and volcanic ash appear sporadically (Teruggi 1954). Quartz, plagioclase and potassium feldspar with variable amounts of amorphous silica such as volcanic glass, appearing micas and opaque minerals are the main mineralogical composition (Teruggi 1954).

Methods

A compilation of pre-existing data and information related to the study area (topographical, geological, hydrogeological and satellite images) was done. Climatic characterization was performed with precipitation data analysis from the weather station located in Coronel Vidal town (37°27′31.6″S, 57°43′55.2″W, 28.3 masl). Additional precipitation and temperature data were obtained from three other weather stations, from W to E: “Estancia La Ventura” (37°51′S, 58°39′W, 157.9 masl), “INTA Balcarce” (National Institute of Agricultural Technology in Balcarce city; 37°45′29″S, 58°17′27.4″W, 131.3 masl) and “Mar del Plata Aeropuerto” (Mar del Plata city airport; 37°56′S, 57°35′W, 13.3 masl) (Fig. 1). Evapotranspiration was calculated for these last three stations using the Thornthwaite (1948) method, obtaining the correspondent hydraulic balances.

Twenty-two sampling campaigns were carried out between October 2010 and October 2012. Groundwater was sampled from 144 wells, and sixteen of these were repeated on different dates to verify that non-important composition variations occur. Twenty-one streamwater samples were collected every 2–3 months, and seven samples from the Mar Chiquita lagoon were taken in just one campaign. These were used for hydrochemical analyses and stable isotopic determinations (^{18}O and ^{2}H). Temperature, pH, electrical conductivity (EC) and alkalinity were determined in situ in each sampling point, and every sample was located through a global positioning system (Garmin eTrex Vista GPS) (Fig. 1). Ninety-nine piezometric levels were measured with a bipolar electric probe.

Analyses were carried out at the Hydrogeochemistry and Isotope Hydrology Laboratory belonging to the “Instituto de Geología de Costas y del Cuaternario,” Mar del Plata University (Mar del Plata city, Fig. 1). Total hardness was measured, and major ions concentrations were determined in all samples. The standard methods used were as follows: chloride following Mohr method, sulfate by turbidimetry, calcium and magnesium by complexometric titrations with EDTA, sodium and potassium by flame spectrometry, silica by means of silicomolybdate method, nitrate by the brucine method and bicarbonate–carbonate by potentiometric titration. Furthermore, fluorine by the zirconyl chloride method and total iron by spectrophotometry (Hach Drel2800 Ferrover1 method) were done. Chemical determinations were performed following detailed methodology in APHA (1992). Hydrochemical information was analyzed through a general statistical characterization and conventional Piper and Schoeller diagrams (Hem 1992) using AQUACHEM software (Calmbach and Waterloo Hydrogeologic Inc. 2003). PHREEQC software (Parkhurst and Appelo 1999) was used to obtain hydrogeochemical models of the solutions.

Isotopic analyses were performed through laser spectroscopy (Lis et al. 2008) using a DLT-100 liquid water isotope analyzer, automated injection, developed by Los Gatos Research. The results were expressed as δ values in permil (‰), defined as: $\delta = 1{,}000\ (R_s - R_p)/R_p$ ‰, where δ is the isotopic deviation in ‰; S is the sample; P is the international reference; and R is the isotopic ratio (^{2}H/^{1}H, ^{18}O/^{16}O). The standard is Vienna Standard Mean Ocean Water (V-SMOW; Gonfiantini 1978). The analytical uncertainties were ±0.2 ‰ for δ^{18}O and ±2.0 ‰ for δ^2H. Monthly precipitation isotopic data obtained from three rainfall stations located, from W to E, in San Manuel town (37°47′18.9″S, 58°50′50″W, 183.8 masl), "INTA Balcarce" (37°45′47.4″S, 58°17′51.7″W, 121.5 masl) and "Facultad de Ciencias Exactas y Naturales (FCEyN)" (38°0′20.3″S, 57°34′16″W, 15.1 masl) (Mar del Plata University, Mar del Plata city) were used (Fig. 1).

In order to facilitate data handling and ensure reliability, a geographical database managed with GIS tools (ArcGis 9.3; ESRI 2007) was used. The digital elevation model (DEM) of the southeastern Buenos Aires province was obtained from digitized and improved topographical maps on a 1:50,000 scale by means of 15-m resolution ASTER images. It allowed both the calculation of basin slopes and the determination of the observation points' altitude. On the basis of these topographical maps, surface water divides were also delimited in the study area, and isovalue contour maps of piezometric level and EC were drawn up to identify different sectors within the zone. Piezometric and EC contours have been obtained through automatic interpolation of groundwater levels measurements and groundwater EC values, applying the inverse distance-weighted method.

Results

Climatic characterization and groundwater flow path

In the weather station situated in Coronel Vidal town, the highest precipitation was observed in February and the lowest one in July, within the period 2000–2009. Annual mean rainfall ranged from 701.5 mm/year in 2008 to 1,443.4 mm/year in 2002, with an average of 1,011.4 mm/year. In the other three weather stations ("Estancia La Ventura," "INTA Balcarce" and "Mar del Plata Aeropuerto"), and for a broader time period (1971–2007), the highest precipitation occurred in December and January and the lowest one between June and August. Annual accumulated rainfall ranged between 491 mm/year (1989, "Mar del Plata Aeropuerto") and 1,342.2 mm/year (2002, "INTA Balcarce"), with an average value of 936.5 mm/year (Fig. 3). Moreover, the temperature records from these last three stations (1995–2007) showed an annual mean value of 13.6 °C. July was the coldest month, with a minimum average recorded in "Estancia La Ventura" (5.6 °C), and January the warmest, with a maximum average recorded in "INTA Balcarce" (20.9 °C) (Fig. 4). In July 2007, the coldest day was recorded at these three weather stations, with a minimum daily mean value of 2.7 °C ("Estancia La Ventura"). On the other hand, in January 2000 the hottest day was recorded, with a maximum daily mean value of 22.7 °C ("INTA Balcarce"). The lowest temperature values were registered in "Estancia La Ventura," possibly due to its location in a geomorphologic environment on average with higher altitudes than in the rest of the study area, where the other weather stations are situated.

The greatest water excess of precipitation over evapotranspiration (1995–2000) occurred in "Estancia La Ventura" between April and November, with a value of 195.5 mm. During December, January and March, when evapotranspiration was greater than precipitation, a water requirement was created to complete the potential evapotranspiration values, which were covered by the soil reserve. Moreover, the total annual values were 696 mm for evapotranspiration and 891.7 mm for precipitation. This station is followed by "Mar del Plata Aeropuerto," with an excess value of 168.4 mm between April and November, and evapotranspiration exceeding precipitation in December, January and March. The total annual values were 724.5 mm for evapotranspiration and 892.9 mm for precipitation. Finally, the lowest water excess took place in "INTA Balcarce" station, with a value of 94 mm between June and November, evapotranspiration being (total value: 737.7 mm) greater than precipitation (total value: 831.6 mm) between December and March and in May. According to these balances, water excess during the winter period is in the order of 150 mm/year and it constitutes the water of the aquifer's recharge and runoff.

Figure 5 shows that the topographical slope in the study area ranges between 1 and 45.5 %. A mean slope of 1.16 % with a standard deviation of 2.20 was obtained. The steepest slope zones are restricted to the range and in the southwest of the hills area, but in most of the catchment, slopes values are below 1 %, occupying the rest of the hills zone and the plain. The distribution of the obtained piezometric contour lines reveals the existence of a regional flow originating in the southwest, near Balcarce's mountains and heading toward the northeastern area and ending toward the Mar Chiquita lagoon. The direction of the flow lines demonstrates that zonal creeks are mostly gaining streams. Moreover, the highest hydraulic gradient values (approx. 0.003) are located in the southwest, close to the mountain range, gradually decreasing to the northeast (approx. 0.001), as one moves toward the coast (Fig. 5).

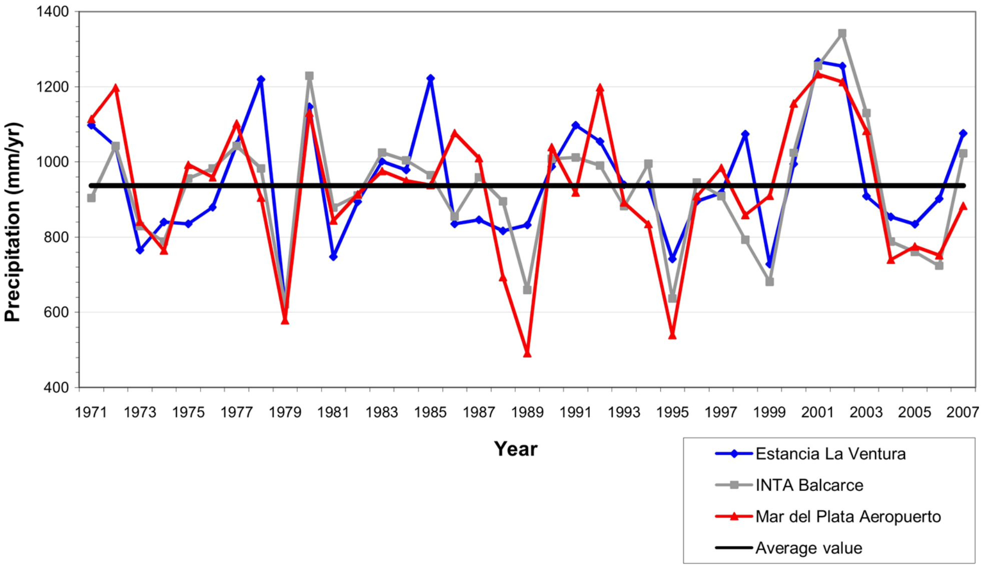


Fig. 3 Period 1971–2007. Annual accumulated precipitation values and its average (mm/year) for "Estancia La Ventura," "INTA Balcarce" and "Mar del Plata Aeropuerto" weather stations

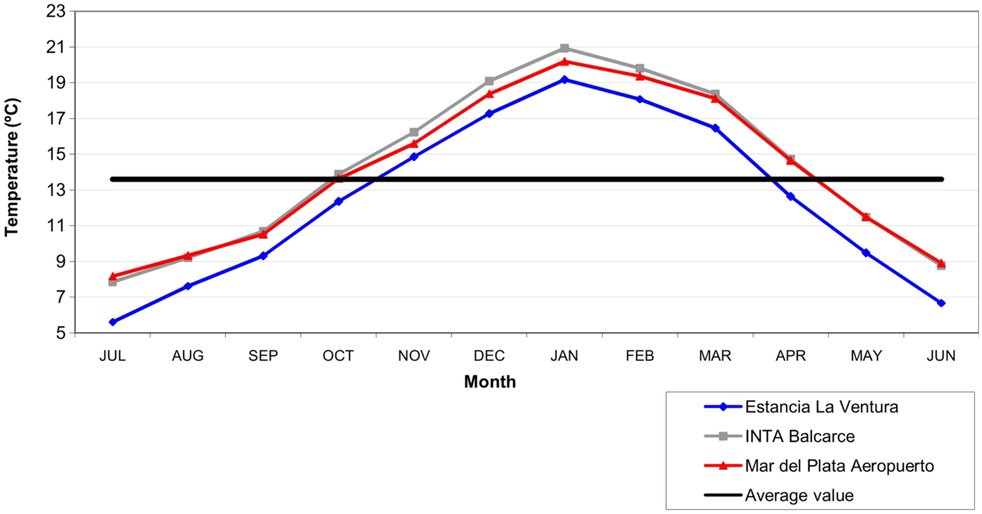


Fig. 4 Temperature monthly mean values and annual average (°C) (period 1995–2007) for "Estancia La Ventura," "INTA Balcarce" and "Mar del Plata Aeropuerto" weather stations

Hydrochemical characterization

Groundwater pH mean value is 7.4 indicating slight alkalinity. The temperature has an average value of 16.5 °C, ranging from 13.6 to 22.2 °C. The EC varies between 419 and 8,180 µS/cm and has an average value of 1,514.5 µS/cm (Table 1). This parameter shows a regional SW–NE increase, in accordance with flow direction (Fig. 5). Three evolutionary areas were determined through automatic interpolation of groundwater EC field measurements within the aquifer, applying the inverse distance-weighted method (Fig. 6). The first one, located in the southwest, was identified as a recharge area, keeping in mind the predictable behavior of the hills geomorphologic zone. The EC contour line of 1,000 µS/cm approximately coincides with the boundary between hills and the fluvial–eolian plain. The second one was identified as a transit area, and it is mostly placed in the middle sector, with an EC range of 1,001–2,600 µS/cm. The third, defined as a discharge area, is located to the northeast and has an EC boundary of 2,600 µS/cm. Considering that both zones, transit and discharge, are situated within the same geomorphologic zone of fluvial–eolian plain, the EC limit among them was determined as the result of adding the standard deviation to the EC average value. Moreover, as it can be observed in Fig. 6, there is a smaller transit sector located in the southwest of the study area, whose EC values are higher than 1,000 µS/cm (ranging from 1,040 to 1,620 µS/cm). This may be due to its location within the up-stream floodplain zone placed between Balcarce city and El Volcán Mountain Range (Fig. 1).

Groundwater ionic composition is variable. The hydrogeochemical facies analysis (Back 1961) conducted by a Piper diagram allows a general classification as sodium

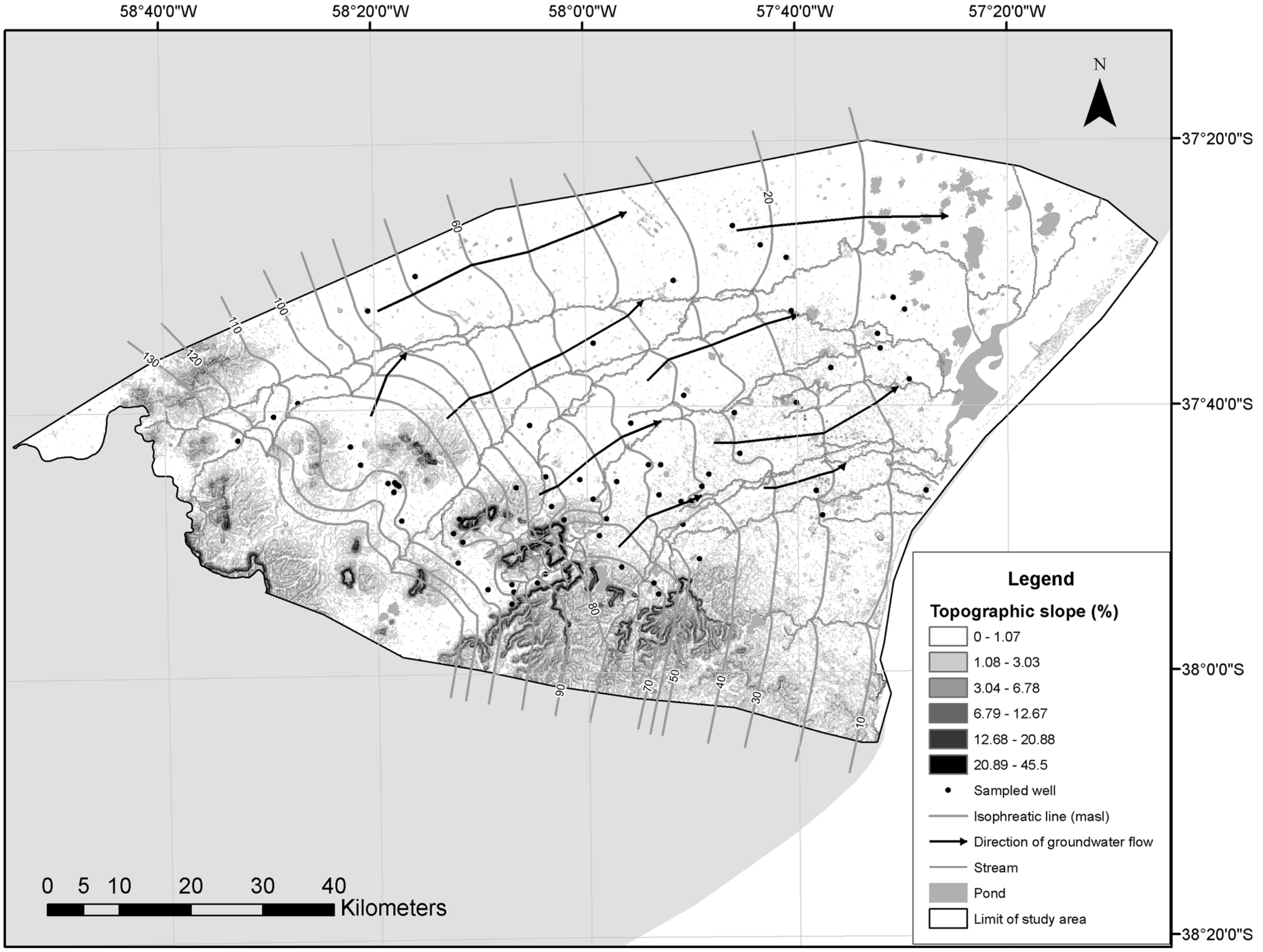


Fig. 5 Piezometric map and topographical slope of the study area

Table 1 Statistical parameters of groundwater composition

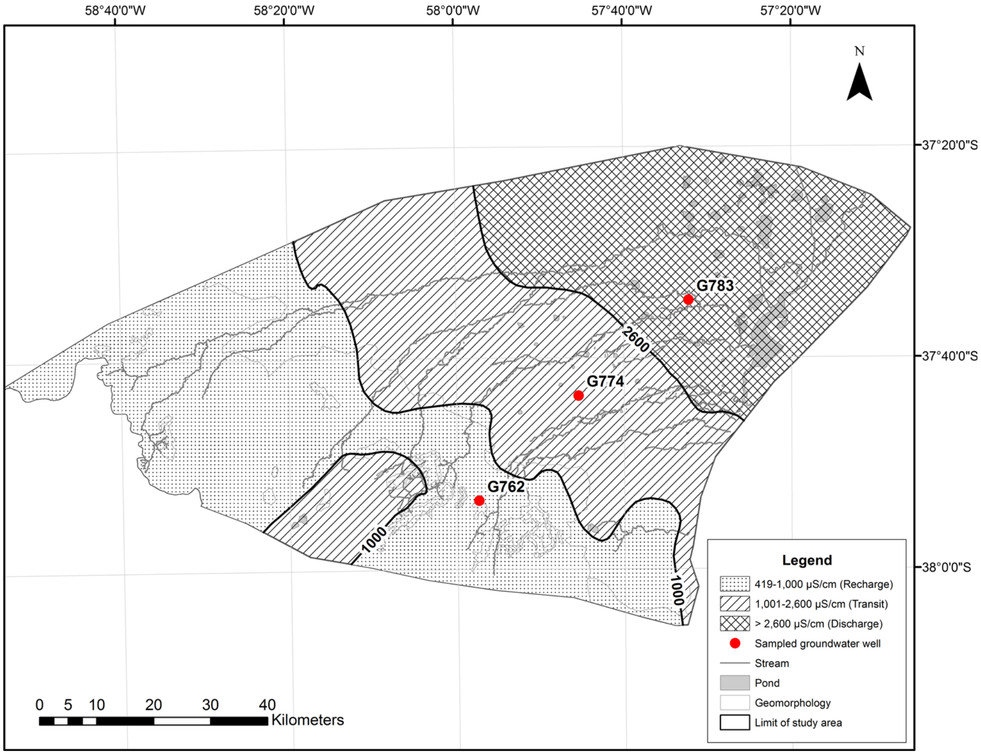
Parameter	Unit	Min	Max	Average	SD	Sample num.
pH		7.0	8.8	7.4	7.7	125
T	°C	13.6	22.2	16.5	1.2	120
EC	µS/cm	419.0	8,180.0	1,514.5	1,145.9	125
Ca^{2+}	mg/l	10.5	490.0	48.4	66.4	116
Mg^{2+}	mg/l	2.5	570.4	54.7	72.3	116
Na^{+}	mg/l	30.0	1,200.0	306.5	222.8	116
K^{+}	mg/l	0.8	100.0	19.2	13.4	107
Cl^{-}	mg/l	23.7	3,235.4	242.5	428.3	116
HCO_3^{-}	mg/l	308.0	1,566.0	763.2	228.9	116
SO_4^{2-}	mg/l	7.6	1,550.0	119.9	215.2	114

T temperature, *EC* electrical conductivity, *SD* standard deviation

bicarbonate (Fig. 7a). Sodium is the dominant cation, whose values vary between 30 and 1,200 mg/l, with an average value of 306.5 mg/l. As for the anions, bicarbonate predominates, and its concentration ranges from 308 to 1,566 mg/l, with an average value of 763.2 mg/l (Table 1). Some samples taken near Balcarce town, El Volcán Mountain Range and La Brava pond, within the Tandilia System (Romanelli et al. 2010), are magnesium bicarbonate type. For the plain environment, a few samples sited close to Vivoratá and Coronel Vidal towns (Fig. 1) are sodium–sulfate–chloride type; while near the Mar Chiquita lagoon, they are magnesium chloride type. Consequently, the analysis yielded a gradual increase in chloride, sulfate and magnesium concentrations, and a bicarbonate decrease along the flow path from the range sector to the coastal area.

In order to get a better conceptual model of the hydrogeochemical evolution in groundwater, a set of samples along a transect from recharge to discharge areas (from wells G762, G774 and G783; Fig. 6) was represented in a Schoeller diagram (Fig. 8). A main trend toward increasing salinity could be observed. This was mostly followed by chloride and sulfate concentrations, while bicarbonate

Fig. 6 Zones defined from groundwater EC values



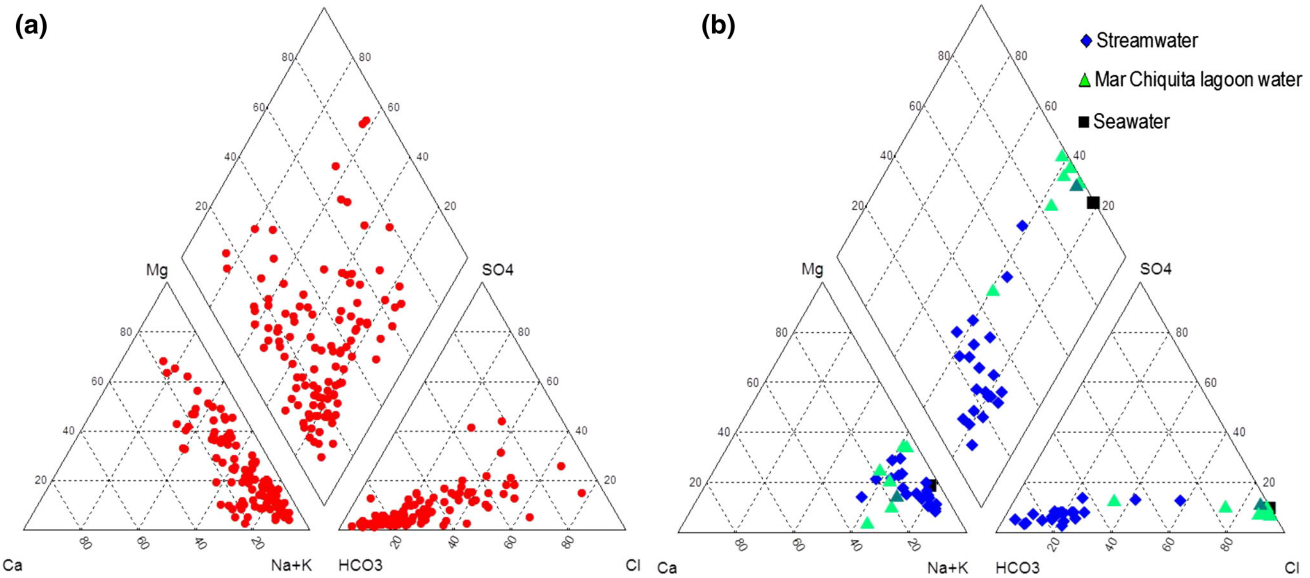


Fig. 7 Ionic composition **a** groundwater, **b** surface water

remained quite constant, as could be expected in phreatic aquifers and/or in areas where calcite equilibrium prevails. Also, sodium increased in the flow direction and calcium and magnesium showed a less noticeable increasing trend toward the discharge area too.

Figure 7b shows the ionic composition of streamwater and the Mar Chiquita lagoon water, including seawater. Streamwater has a homogeneous ionic composition, being sodium bicarbonate type. Sodium is the dominant cation, whose values vary between 160 and 470 mg/l, with an average value of 296.1 mg/l. Bicarbonate is the predominant anion, with values ranging from 350 to 1,067.2 mg/l and with a mean value of 692.9 mg/l. There are two samples located at the lagoon discharge zone that are of magnesium chloride type. Temperature values range from 10.1 to 24.8 °C; this parameter average value being

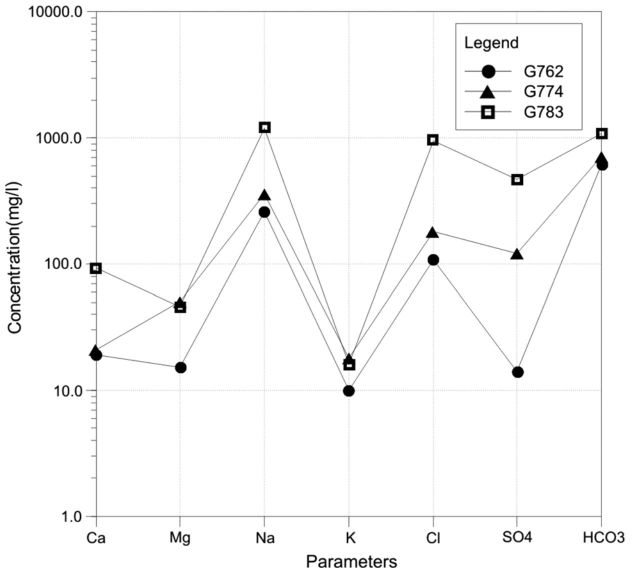


Fig. 8 Schoeller diagram of groundwater samples along a transect from recharge to discharge area

Table 2 Statistical parameters of streamwater composition

Parameter	Unit	Min	Max	Average	SD	Sample num.
pH		7.7	9.5	8.3	8.4	21
T	°C	10.1	24.8	18.7	5.1	21
EC	µS/cm	795.0	2,020.0	1,121.0	309.7	21
Ca^{2+}	mg/l	15.0	95.0	38.0	23.4	21
Mg^{2+}	mg/l	21.0	67.0	35.6	13.2	21
Na^{+}	mg/l	160.0	470.0	296.1	74.5	21
K^{+}	mg/l	12.0	32.0	18.9	5.8	20
Cl^{-}	mg/l	29.4	487.0	125.0	113.4	21
HCO_3^{-}	mg/l	350.0	1,067.2	692.9	191.1	21
SO_4^{2-}	mg/l	13.0	170.0	56.0	40.3	21

T temperature, *EC* electrical conductivity, *SD* standard deviation

18.7 °C. The mean value of pH (8.3) indicates that the water is of a moderate alkalinity. EC has an average value of 1,121 µS/cm, varying between 795 and 2,020 µS/cm (Table 2). Meanwhile, in Fig. 7b, Mar Chiquita lagoon water shows an increase in its chloride concentration and a decrease in bicarbonate from its north to its south part. Samples taken from the lagoon mouth (south part) have an ionic composition very similar to seawater. Sodium is the predominant cation, with values ranging from 300 to 4,800 mg/l, with a mean value of 2,822.9 mg/l. Chloride is the dominant anion; its concentration varying between 262 and 12,694 mg/l, with an average value of 7,034.1 mg/l. Temperature values range between 19.7 and 27.0 °C, and this parameter mean value is 22.2 °C. The pH average value is the same as in streams. EC varies from 1,564 to 38,350 µS/cm, with a mean value of 22,166.3 µS/cm (Table 3).

The pH variation between groundwater and streamwater was explained by Glok Galli et al. (2012), performing direct hydrogeochemical modeling with PHREEQC. An increase of about two units in pH was obtained as a result, from values near to 7 to values of around 9. This is due to the P_{CO2} (carbon dioxide partial pressure) decrease when groundwater discharges into streamwater, and a P_{CO2} change occurs due to its re-balancing in accordance with atmospheric or similar conditions.

Hydrogeochemical modeling

The same set of samples from recharge to discharge area (from wells G762, G774 and G783; Fig. 6) represented in a Schoeller diagram of Fig. 8 was used to identify main geochemical processes in groundwater evolution, through inverse modeling with PHREEQC. Initially, a sample of the "INTA Balcarce" rainfall station (Fig. 1) was submitted to an evaporation process (by H_2O subtraction from the solution) until obtain recharge water having the chloride content of the sample G762. The resulting solution from the evaporation simulation is taken as the effective recharge water composition entering throughout the non-saturated zone. The obtained evaporation rate (Cl^- concentration in G762/Cl^- concentration in rain water) was 14.7. Then, three inverse hydrogeochemical models were carried out, accepting an analytical error variable between 5 and 15 %. Calcite, $CO_{2(g)}$, gypsum, halite and ionic exchange of Ca^{2+}, Mg^{2+}, Na^+ and K^+ were taken into account as reactant phases (Table 4). These were selected considering that: (1) The Pampeano aquifer is a phreatic aquifer, which means it is open to the atmosphere; (2) the texture of the sediments includes clay size, which provokes higher exchange capacity; (3) the $CaCO_3$ in outcropping sections is abundant; and (4) former detailed studies were performed in the area by Martínez and Bocanegra (2002).

A first inverse model was carried out beginning with the recharge water as the initial solution and well G762, which is located in the recharge zone, as the final one. The second was made using wells G762 as the initial solution and G774, situated in the transit area, as the final solution. The last inverse model was performed using well G774 as the initial solution and well G783, which is located in the discharge zone, as the final.

Calcite dissolution and ionic exchange are the main processes along the groundwater flow path. During the first evolution step (recharge to transit zone), calcite is dissolved until equilibrium, which is shown by the saturation index evolving from −0.10 in sample G762 to 0.41 in sample G774. As it can be observed in Table 4, calcium is adsorbed from exchange surfaces while sodium is released

Table 3 Statistical parameters of Mar Chiquita lagoon water composition

Parameter	Unit	Min	Max	Average	SD	Sample num.
pH		7.8	8.8	8.3	8.3	7
T	°C	19.7	27.0	22.2	2.3	7
EC	µS/cm	1,564.0	38,350.0	22,166.3	16,000.6	7
Ca^{2+}	mg/l	20.0	1,320.0	676.0	554.4	7
Mg^{2+}	mg/l	21.1	1,081.0	474.1	388.7	7
Na^{+}	mg/l	300.0	4,800.0	2,822.9	1,956.6	7
K^{+}	mg/l	34.0	360.0	206.3	137.7	7
Cl^{-}	mg/l	262.0	12,694.0	7,034.1	5,107.7	7
HCO_3^{-}	mg/l	219.0	678.0	402.3	158.0	7
SO_4^{2-}	mg/l	130.0	1,920.0	938.6	648.1	7

T temperature, *EC* electrical conductivity, *SD* standard deviation

Table 4 Reactant phases values (mmol/l) obtained as result in PHREEQC software outputs

Mineral phase	IS RW	FS G762	IS G762	FS G774	IS G774	FS G783
Calcite	2.98		1.16		3.21	
CO_2(g)	−6.19		0.85		5.36	
Gypsum	−0.89		1.10		3.96	
Halite			2.38		23.18	
CaX2	−4.04		−2.22		−5.5	
MgX2	−0.34		1.36		−0.14	
NaX	8.99		1.51		11.33	
KX	−0.23		0.20		−0.05	

IS initial solution, *FS* final solution, *RW* recharge water

according to the selective order of exchange surfaces in the normal geochemical evolution (Chebotarev 1955). The strong Ca^{2+} adsorption involved in the different steps (between 2.2 and 5.5 mmol/l adsorbed) allows the sustainability of the calcite dissolution during all the hydrogeochemical evolution. Halite dissolution is the process that is included to explain the chloride concentration increase in the flow direction. It involves the salinity increase by the longer contact time to the mineral phase plus the continuous input from the non-saturated zone when infiltration leaches the precipitated salts.

As a result of the described processes, groundwater evolves from low salinity calcium–magnesium bicarbonate waters to high salinity sodium bicarbonate waters, with few samples being sodium-chloride type. Atmospheric CO_2, calcium carbonate concretions in the sediments and marine aerosol concentration are the main sources of dissolved solids, while chemical equilibrium and cationic exchange are the main processes.

Isotopic characterization

The results of isotopic determinations performed on 93 groundwater samples, 18 streamwater samples and 6 Mar Chiquita lagoon water samples were plotted on a conventional diagram δ^2H versus $\delta^{18}O$, together with the global (GMWL) and local (LMWL) meteoric water lines. The LMWL was obtained from isotopic data of 91 precipitation samples of the rainfall stations located, from W to E, in San Manuel town, “INTA Balcarce” and “Facultad de Ciencias Exactas y Naturales (FCEyN)” (Mar del Plata University, Mar del Plata city) (Fig. 1). This is given by the equation δ^2H ‰ $= 8.3\delta^{18}O + 16.3$. The weighted stable isotopes composition for precipitation ranges from −12.59 to −0.76 ‰, with an average value of −5.42 ‰ for $\delta^{18}O$, and from −95.3 to 15.4 ‰, with a mean value of −28.7 ‰ for δ^2H. In addition, the streams and Mar Chiquita lagoon trendlines were obtained (Fig. 9).

Groundwater samples appear grouped in the graph showing relatively constant isotope composition, close to the average precipitation composition. This fact indicates that it is a well-mixed system from rainwater. These samples have stable isotopes values ranging between −5.76 and −0.79 ‰, with a mean value of −4.73 ‰ for $\delta^{18}O$, and between −32.0 and −2.6 ‰, with an average value of −25.4 ‰ for δ^2H. Moreover, there are two groundwater samples disposed along the streams trendline (G460 and G797; Fig. 9) with enriched $\delta^{18}O$ and δ^2H values. Groundwater isotopic data can also provide a reliable determination of the recharge area (Clark and Fritz 1997), but in this catchment, the altitude and continental effects were not observed, and consequently, isotopic deviation does not provide sufficient differences in order to be useful for this purpose.

Streams isotope composition is similar to groundwater having lower clustering, with values ranging between −4.95 and −0.65 ‰ for $\delta^{18}O$, and −26.7 and −0.9 ‰ for δ^2H, and with average values of −3.82 ‰ for $\delta^{18}O$ and −20.7 ‰ for δ^2H. Some samples are along a line corresponding to the equation δ^2H ‰ $= 6\delta^{18}O$ ‰ $+ 2.2$, which cannot be attributed to an evaporation line because the slope is higher than the expected values around 5 or less.

Mar Chiquita lagoon samples show a progressive enrichment in their isotope composition from the north of

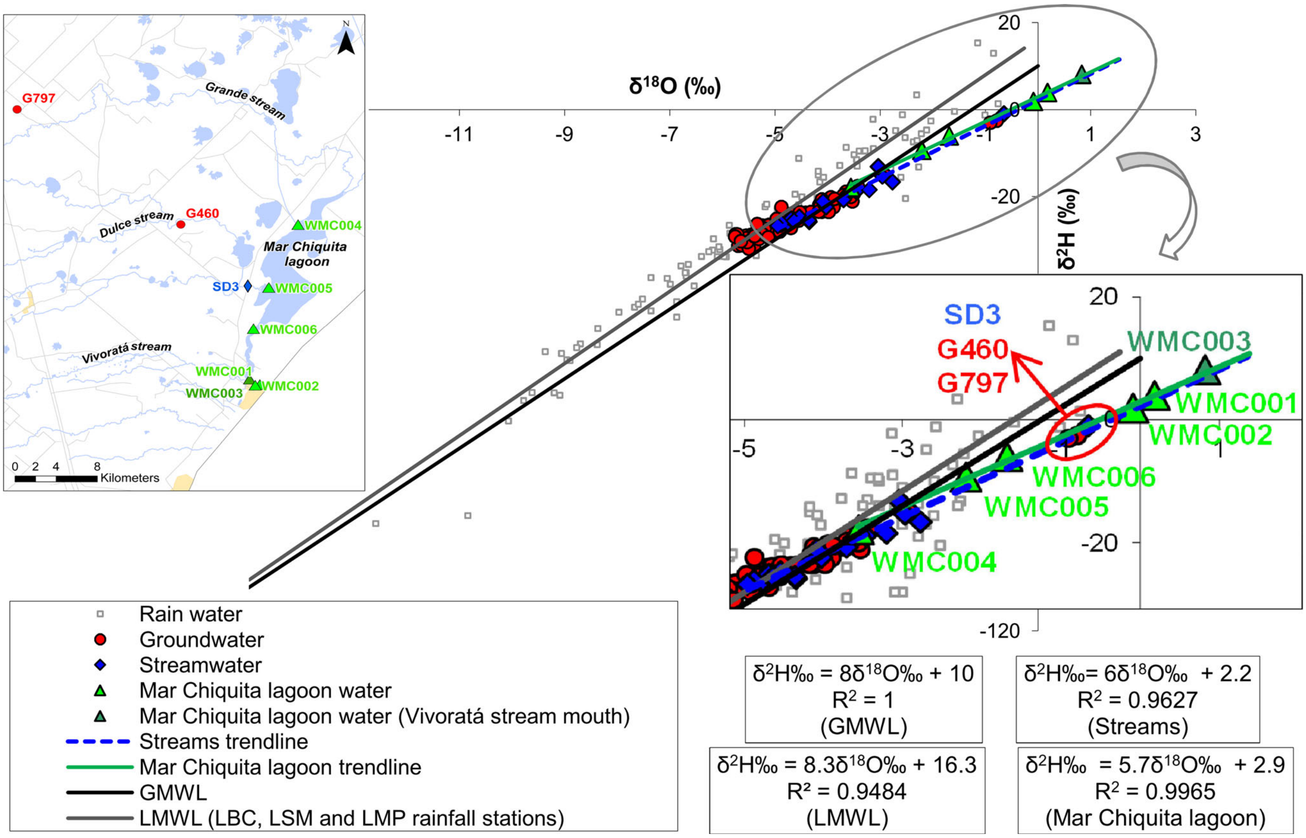


Fig. 9 Isotope composition (δ^2H and δ^{18}O) of precipitation, groundwater, streams and Mar Chiquita lagoon

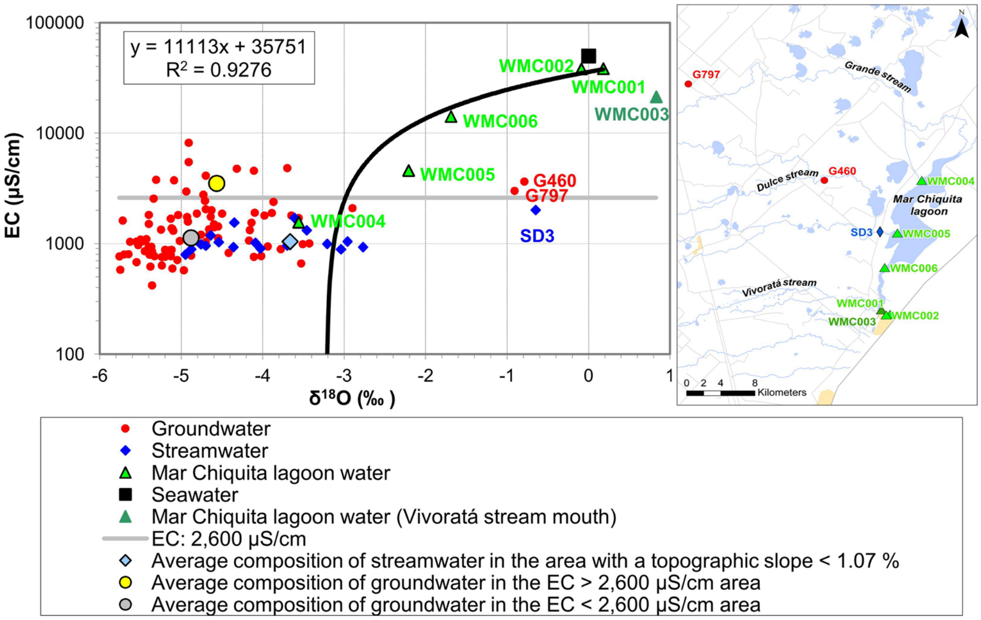
the lagoon to its mouth area, located in the south. The samples placed southward (WMC001 and WMC002) show an almost seawater stable isotope composition ($\delta^{18}O = 0$ and $\delta^2H = 0$). The water sample taken at the Vivoratá creek outlet into the lagoon (WMC003) is the more enriched (Fig. 9). These lagoon water samples are disposed along a trendline from the LMWL toward seawater composition. This line shows an equation with a slope value of about 6 (δ^2H ‰ $= 5.7\delta^{18}O$ ‰ $+ 2.9$) being a mixing line, which is typical in a coastal lagoon system with estuarine behavior.

Groundwater, streamwater and Mar Chiquita lagoon water were represented in a scatter diagram of EC versus δ^{18}O, including seawater composition (Fig. 10). A logarithmic scale was used to plot the EC (µS/cm) on the vertical axis, to include the broad range of values of this parameter. In general, within the composed field of values between 400 and 10,000 µS/cm EC and below −2.6 ‰ for δ^{18}O, most of the groundwater and streamwater samples are grouped and the latter with a lower clustering. Otherwise, as can be seen in Fig. 10, two groundwater samples (G460 and G797) and a streamwater sample (SD3) (with enriched δ^{18}O and δ^2H values, Fig. 9) are placed within the field whose boundaries range between 2,000 and 4,000 µS/cm EC and −1.2 and −0.6 ‰ for δ^{18}O. The Mar Chiquita lagoon sample located in the northern part (WMC004) also falls in the range of most groundwater and streamwater sampling points. Samples taken at the mouth area (WMC001 and WMC002) are plotted near the seawater composition, with EC values of around 30,000 µS/cm and between −0.2 and 0.4 ‰ for δ^{18}O. The lagoon sample taken at the Vivoratá stream outlet zone (WMC003) has a more dilute composition (lower EC: 20,000 µS/cm) in regard to the other samples located at the lagoon mouth, and this is the sample that is more enriched in ^{18}O content (around 0.8 ‰) (Fig. 10). So, in general, the Mar Chiquita lagoon samples from north to south tend to be similar to seawater composition both in EC contents as in the δ^{18}O, as shown by its trendline.

Discussion

Mar Chiquita lagoon receives saltwater and freshwater inputs, as any coastal lagoon showing estuarial behavior. The proposed hydrogeochemical evolution model starting from rain water can explain the groundwater's ionic

Fig. 10 Scatter diagram (EC vs. $\delta^{18}O$) for groundwater, streams, Mar Chiquita lagoon and seawater



composition evolution, taking into account an equilibrium with calcite in an open system and cationic exchange processes, as was also observed in other studies for the Pampeano aquifer (Bonorino et al. 2001; Martínez and Bocanegra 2002; Quiroz Londoño et al. 2008). Compact calcite concretions widespread in the whole plain play an important part in water chemical quality.

Significant reactions take place after rainwater infiltration, from the recharge area toward the discharge zone, modifying the groundwater chemical composition. These changes are very important because they determine groundwater composition in discharge areas. Magnesium–calcium bicarbonate water predominates in the hilly area close to the mountains, because infiltrated rainwater equilibrates with carbonates and dissolves the less stable silicates present in the loess. Cationic exchange defines the evolution toward sodium bicarbonate or sodium–sulfate–chloride waters. The anionic composition is modified by the carbonate equilibrium control on inorganic dissolved carbon. On the other hand, this can also be affected by the soluble salts addition (NaCl, $CaSO_4$ and Na_2SO_4) that are present as powder in the loess matrix due to water evaporation in the non-saturated zone. As a result, groundwater discharging into streams is mainly sodium bicarbonate water, despite sodium-chloride compositions can be observed in some points (Massone et al. 2005).

Stable isotope data show that groundwater has a composition that approximates the average isotope composition of regional rainfall. Therefore, groundwater represents a well-mixed system since its content is relatively homogeneous (Gat and Tzur 1967), which could be assimilated to a dispersive model. Streamwater samples have, in turn, a similar isotopic signature to groundwater, showing an important baseflow domain into the creeks' flow, but with a greater variation along the water meteoric line, indicating a seasonal temperature effect on runoff. The line slope for streamwater samples is not consistent with an evaporation process, and a correlative increase in EC is not observed (Figs. 9, 10). The probable explanation is that enriched rains form part of the streamwater as channel interception water. Values of $\delta^{18}O$ in the order of -2 ‰ were determined at "FCEyN" and "INTA Balcarce" rainfall stations (Fig. 1) when enriched streamwater samples were collected. The case of groundwater samples G460 and G797 is different as they could not be affected by channel precipitation. For these, and also for sample SD3, the accompanying increase in EC suggests local evaporation as a possible explanation (Figs. 9, 10).

Mar Chiquita lagoon samples are disposed in Fig. 9 along a trendline from the LMWL toward seawater composition (0, 0) that can be taken as a mixing line. The lagoon sample located at the Vivoratá stream mouth zone shows a more dilute composition (lower EC) compared with the other lagoon samples located to the south, and the more enriched $\delta^{18}O$ value (Figs. 9, 10). This indicates the Vivoratá creek discharge effect, water being less saline than seawater but highly isotopically enriched, due to evaporation.

Using all the available data in order to account for the hydrological lagoon budget, it is possible to apply some end members identification, following the concepts of Christophersen et al. (1990), Hooper (2003) and Vázquez-Suñé et al. (2010), among others. For this proposal, the EC versus $\delta^{18}O$ graph (Fig. 10) is a useful tool. Three main components can be recognized as end members in the Mar Chiquita coastal lagoon: seawater on one hand and freshwater contribution, which includes streamwater and also direct groundwater discharge, on the other. The representative composition of the three end members in the Mar Chiquita lagoon water budget is shown in Fig. 10: the seawater composition, the average composition of 10 streamwater samples located in the area with a topographical slope below 1.07 % (Fig. 5) and the mean composition of 18 groundwater samples taken in the zone where EC values are above the limit of 2,600 µS/cm, i.e., groundwater discharge into the lagoon. For the calculation of these average compositions, the outlying samples G460, G797 and SD3 were not taken into consideration. Moreover, the average composition of 73 groundwater samples situated in the recharge and transit areas was plotted as a comparison reference.

Looking at the three end members that were indicated in Fig. 10 and the distribution of the samples in this graph, it is clear that lagoon water sampling points are disposed along a trendline having in its extremes seawater and streamwater compositions. The mean content for EC and δ^{18}O of the groundwater located in the discharge zone falls outside the line, indicating a small contribution to the lagoon. The average composition of streamwater entering into the lagoon corresponds to the groundwater discharge in the upper and middle sections of the catchment, which has a lower salinity (EC from around 420 to 2,100 µS/cm) than groundwater in the distal zone (EC from about 2,600 to 8,100 µS/cm). Therefore, the EC value of the northern lagoon sample (WMC004, 1,564 µS/cm) cannot be attributed to the contribution of groundwater in the discharge zone (EC average value = 3,516 µS/cm).

Despite the piezometric map of Fig. 5 shows the groundwater flow direction toward the northeastern area of the catchment, the extremely low hydraulic gradient toward the Mar Chiquita lagoon results in a very slow flow rate and consequently small discharge. It could be negligible against the faster streamwater input into this coastal lagoon. Taking into account a hydraulic conductivity of 10 m/day (Martínez and Bocanegra 2002; Lima et al. 2013) and the obtained hydraulic gradient for the flat zone, a groundwater flow velocity of about 0.01 m/day can be estimated. Groundwater residence times around 30–50 years obtained through CFCs measurements in the plain catchment area (Martínez et al. 2013) also support the idea of the slow flow rate and small discharge.

The other water supply, seawater, is due to the lagoon estuarine behavior and depends on the distance to the mouth and the tidal cycles. Thus, taking into account the average EC of the groundwater located in the discharge zone, its direct contribution to the lagoon was minimized, considering streamwater and seawater as the two dominating end members. Their proportion at different points of the lagoon can be obtained by using the lever rule in the EC versus δ^{18}O scatter diagram, taking into account an excellent linear regression ($R^2 = 0.9276$). In this way, it is possible to calculate that about 84 % of the water in the lagoon sample WMC001 is coming from seawater, as well as the 82 % in WMC002, 33.5 % in WMC006, 15.4 % in WMC005 and 0 % in WMC004. The outlying lagoon sample WMC003 was not included in the calculation of this mixing line.

Conclusions

Groundwater and streamwater are closely interacting in the Mar Chiquita's lagoon catchment. These waters are mostly sodium bicarbonate type, while the lagoon chemical composition shows an evolution toward seawater composition, from the north to its mouth, located southerly. Local groundwater systems outflow into streams, and water composition is mainly modified by a reduction in a partial pressure of CO_2. There is a close relationship between the present hydrogeochemical phases and the geomorphology. The mountain ranges and hills systems are the recharge zone determining the isotopic fingerprint and the origin in the hydrogeochemical evolution.

The average isotope compositions of groundwater (−4.73 ‰ for δ^{18}O and −25.4 ‰ for δ^{2}H) and precipitation in the region (−5.42 ‰ for δ^{18}O and −28.7 ‰ for δ^{2}H) are similar, showing an aquifer recharge source from rain infiltration. Streamwater isotope composition is close to groundwater isotope composition, suggesting an aquifer discharge domain into the creeks' flow, as obtained piezometric contours show. Channel interception of heavy rains results in a slightly more enriched streamwater composition. Moreover, Mar Chiquita lagoon samples showed a progressive enrichment in its isotope composition from the north to its mouth area.

Three main components were recognized as probable end members in the hydrological budget of the Mar Chiquita lagoon: (1) seawater, characterized by sodium-chloride water type, high salinity (EC value of about 50,000 µS/cm) and a defined isotope composition (0, 0); (2) streamwater, whose chemical composition is due to groundwater discharge mainly in the recharge and transit areas, having low salinity (EC value below 2,600 µS/cm) and a more enriched stable isotope composition; and (3) groundwater in the discharge area, which has a similar isotope composition to the former type but is more saline as a consequence of the normal geochemical evolution (EC average value of 3,516 µS/cm).

Having found a way to differentiate streamwater discharge from groundwater direct discharge to the Mar

Chiquita lagoon, it was possible to assign to the probably end members their role in the water budget. The extremely low hydraulic gradient toward the Mar Chiquita lagoon results in a very slow flow rate and consequently a small groundwater discharge. As a consequence of that, obtained EC values for groundwater in the discharge zone allow minimizing its direct contribution and to considering two dominating end members: streamwater and seawater. Their proportions could be obtained for any point at any time from the EC and δ^{18}O parameters using the lever rule in the scatter graph. The calculated proportion will be different in accordance with streams discharge and tidal effects.

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